THESIS

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The author would like to express his gratitude to Professor J.M. Robertson and Dr. G.Thomson of this department who suggested the topics for this thesis, and who guided his steps in the work on them. Thanks are due also to the Senate of the Massachussetts Institute of Technology for allowing some of the calculations to be carried out on their IBM 704 computer.

SUMMARY

Part I

A new photographic method for the measurement of the intensities of X-ray diffraction spectra is described. In principle it is similar to the positive print method, but photographic reversal is used instead of printing. Film processing conditions are given. The accuracy of this method is compared with that of the visual estimation technique.

Part II

Crystallographic studies on three tropolones are described. Using new data, the (hko) projection in copper tropolone was refined. Atomic coordinates and anisotropic thermal parameters were refined by least squares using an IBM 704 computer. The results, while not conclusive, question the regularity of the tropolone ring in this molecule.

A crystallographic study of the (hol) zone of cupric nootkatin was carried out. This zone is completely phase determined. This analysis confirmed the structure proposed earlier by Campbell from a study of the (okl) zone which is not entirely phase determined.

The unit cell dimensions and the space group of β-methyl-tropolone methyl ether are recorded.

There is a unity to the thesis which is not apparent from the above. Part I was undertaken because of conflicting results obtained in the measurements of the intensities from copper tropolone. The new and independent method of measurement decided unambiguously in favor of one of the sets of measurements. This was the set used in the refinement.

CONTENTS

PART I

CONTENTS (contd.)

CONTENTS (contd.)

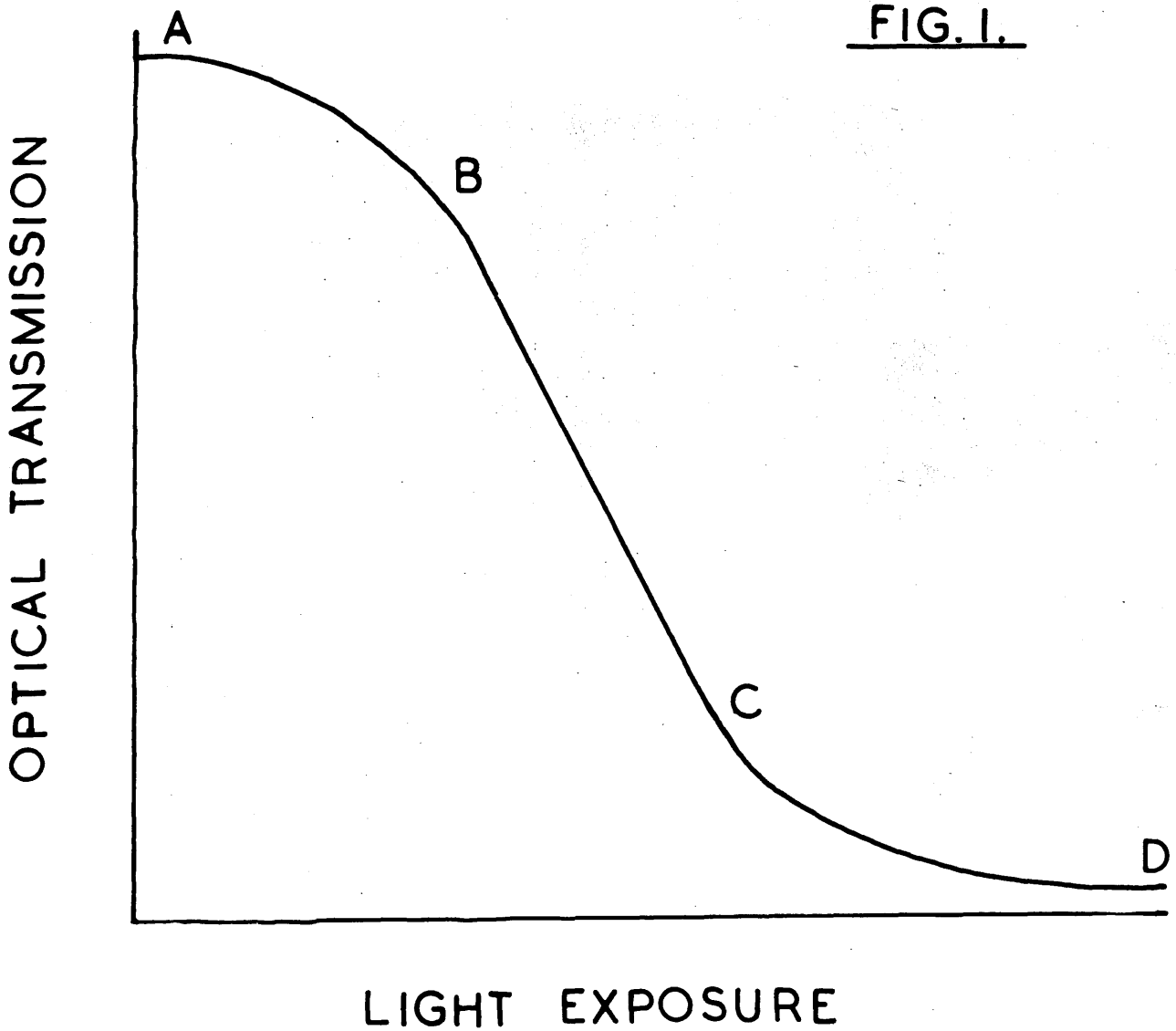
Copper mootkatim

2-Methoxy-6-methyl-tropone

PART I

A New Photographic Process for the Measurement of the Intensities of X-ray Spectra.

FIG. 1.



INTRODUCTION.

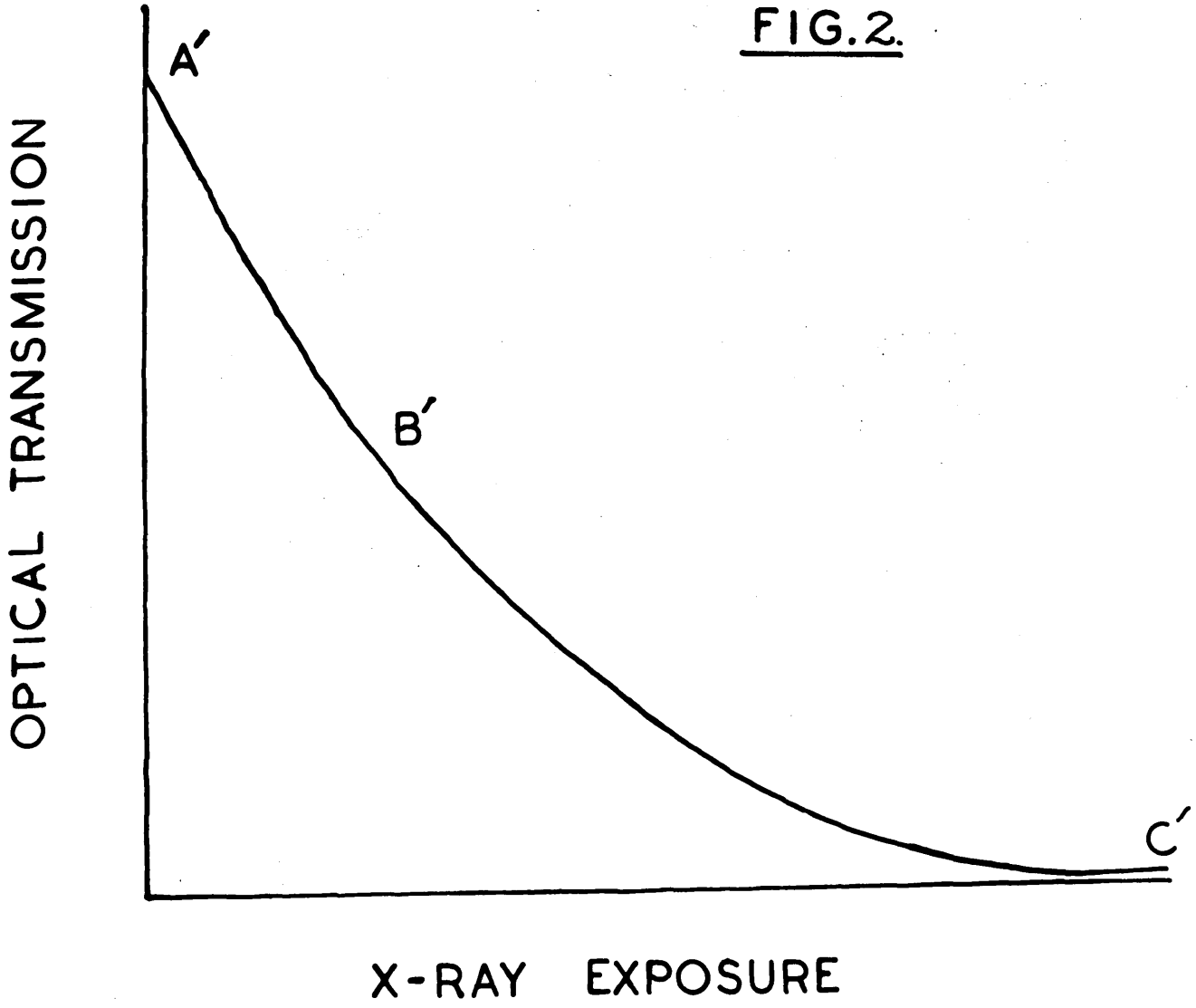
If, on a piece of photographic film, are recorded a number of exposures to radiation such that each exposure is related to the next in a simple way, then a step wedge results. This step wedge can be obtained using a rotating sector. Now, if this radiation is light, and the optical transmission through each step is measured and plotted against the corresponding exposure, then a curve of the form shown in Fig. 1, is obtained. This curve is called the characteristic curve of the film. The optical transmission is defined as the ratio of the amount of light transmitted by the step to the amount transmitted by unexposed film under the same conditions; the ratio is expressed as a percentage.

Over the region BC of the curve, the transmission is directly proportional to the light exposure, It, where I is the intensity of illumination and t is the time of exposure to that illumination. The regions AB and CD represent deviations from this relationship, the well known failure of the Bunsen-Roscoe reciprocity law[1].

Schwarzschild proposed an equation[2],

$$It^p = \text{constant},$$

FIG.2.



where I and t are as before, and p is a constant with a value of 0.8 for visible light. This relationship holds quite well for low light intensities, and describes accurately the portion AB of the curve. However at higher intensities of illumination, p adopts different values.

When X-rays are used, the characteristic curve is of the form shown in Fig. 2. For low values of X-ray intensity, the Schwarzschild constant, p, is unity. It will be observed that the regions AB and BC of the light curve have merged in the X-ray curve to give A'B' which is linear. Beyond B', p is no longer unity; the curve ceases to be linear and proceeds exponentially to a limit, C', corresponding to complete activation of all the silver halide present in the emulsion.

With these photographic details in mind it is possible to review some of the methods which have been used to determine the intensity of X-ray reflections from crystals.

The intensities and relative phases of the X-ray reflections from a crystal are controlled by the number, nature, and spatial arrangement of the atoms in the molecule which form the building units of the crystal. The number and nature of the atoms in the molecule can

generally be found by chemical analysis. X-ray analysis of a crystal of the compound can then give the spatial arrangements of the atoms in the molecule, if the intensities and relative phases of the reflections are known. In general the intensities of the reflections can be directly observed, but not the relative phases.

One of the earliest methods for the measurement of these intensities involves the measurement of the conductivity induced by the reflected X-ray beam in an ionisation chamber[3]. More recent methods use Geiger counters[4], or scintillation counters[5]. Such methods, while accurate, require expensive and delicate equipment, and the ionisation spectrometer method is very slow.

Photographic methods are both cheaper and easier to apply, and they provide a permanent record which is not available from the preceding methods. Visual estimation of the intensities by the multiple film technique is widely used[6]; carefully applied, it can give intensities accurate to within 10%, but is somewhat tedious to use.

Now the image of an X-ray crystal reflection, recorded on a photographic film, is not of uniform

density. The optical transmission varies from point to point in the image in an irregular manner. Therefore the transmission through the point of maximum density of the image does not give a measure of the total amount of radiation reflected by the plane producing the image. It is this latter quantity which is used in crystal structure analysis, and it is called the integrated intensity.

If the photographic image of the reflection on the X-ray negative is considered to be divided into a very large number (n) of small areas, such that each area is of uniform density, then:

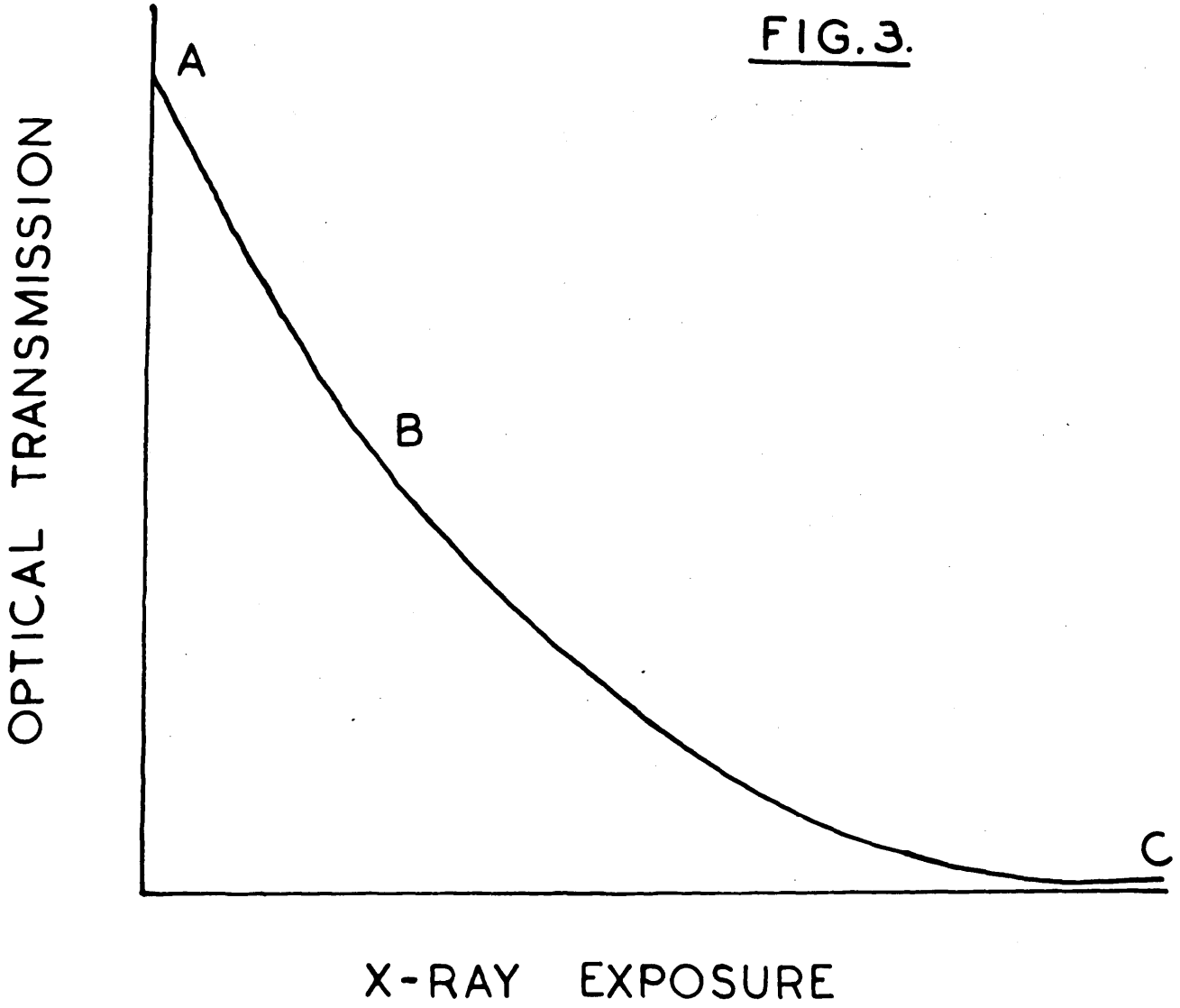
$$\text{Intensity of the } r^{th} \text{ area} = k_r(100 - T_r),$$

where, T_r is the optical transmission through the r^{th} small area, and k_r is a proportionality constant for the r^{th} area.

$$\text{Then, Integrated Intensity} = \sum_{r=1}^{n} k_r(100 - T_r).$$

If the point of minimum transmission in the image lies on the linear portion of the characteristic curve, then all points in the image must lie on that portion

FIG. 3.



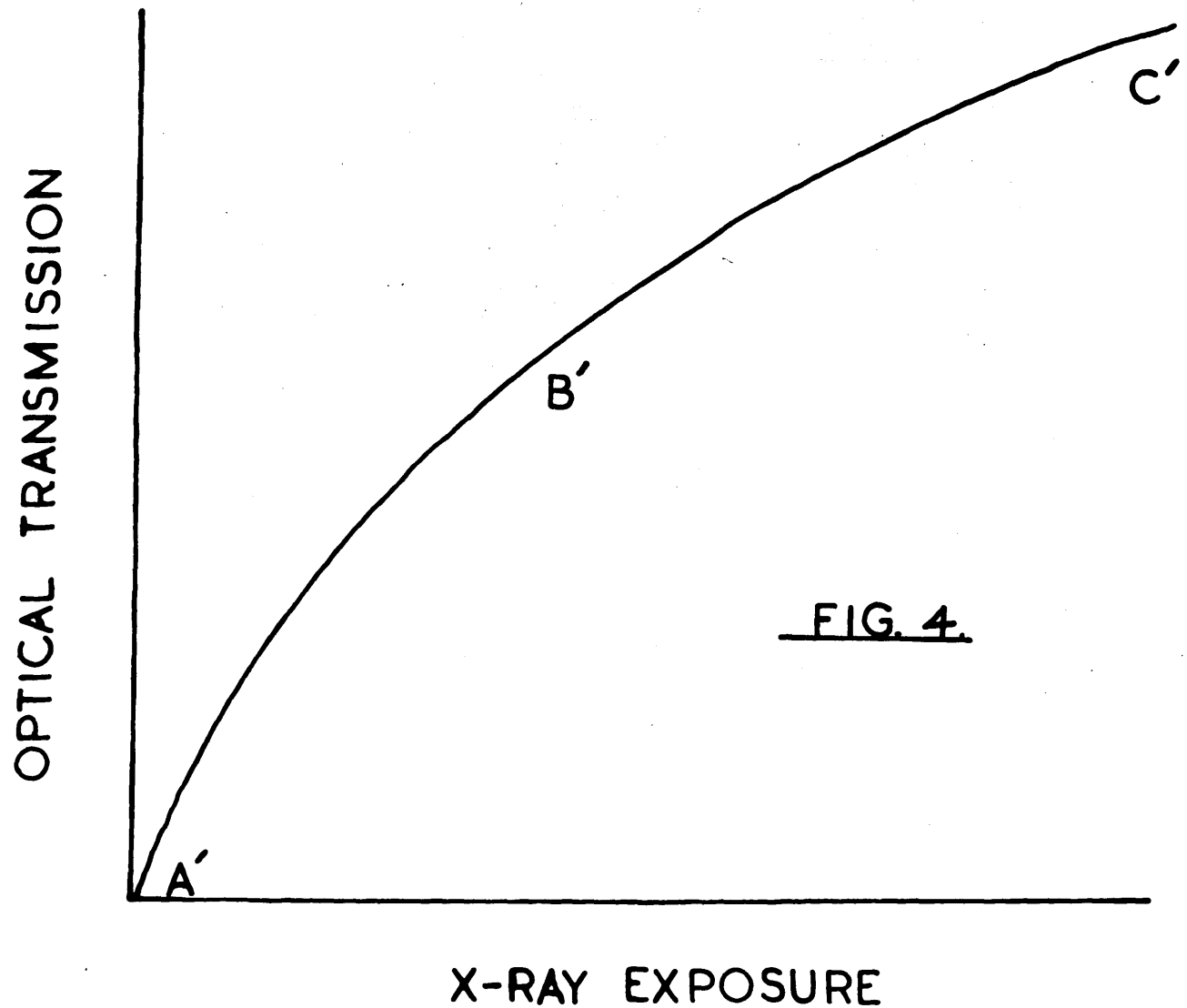


FIG. 4.

(A'B' in Fig. 2). In such a case the constants, k_r, are all equal, and the integrated intensity is then proportional to $\sum_{r=1}^{n} (100 - T_r)$. This is the principle of the visual estimation method of measuring the intensities. A photometric method involving this principle has also been described[7].

Integrating photometers[8] have been devised which measure and sum the individual transmissions through a large number of areas on the negative image of the reflection. These instruments can be calibrated with a standard step wedge superimposed on the photograph, and so are not limited to the examination of reflections whose minimum transmission lies on the linear part of the characteristic curve.

The photographic methods mentioned so far have all made measurements on the X-ray negative. Dawton's positive print method of measuring X-ray intensities[9] integrates in a different way. If Fig. 3 represents the characteristic curve for the X-ray negative, then Fig. 4 should represent the characteristic curve of a positive print made from that negative. Any point in the image which lies on the region AB of the characteristic curve of the X-ray negative will lie on the region A'B' of the characteristic curve of the printed

positive. Similarly any point on BC should lie on B'C' of the printed positive characteristic curve. Now, it should be possible, by controlling the development times of both negative and print, and the printing exposure, to find conditions such that the positive and negative characteristic curves combine to give a resultant linear curve. This Dawton was able to do. Under such conditions the positive characteristic curve departs from linearity only at regions approaching 100% transmission, corresponding to complete activation of the silver halide on the negative film. The integrated intensity of each reflection can thus be obtained by a single photometer reading covering the whole area of the image, unless some part of the image has a transmission of 100%.

Printing, then, offers a rapid and reliable way of measuring a wide range of X-ray intensities. However it has not been widely used. The printing exposure and developing times are critical, and so it is not easy to obtain consistent results.

A positive image may also be obtained by photographic reversal. This consists of normal development followed by removal of the silver formed in the emulsion,

total exposure to light, and a second development. The work described in the following pages was undertaken to determine whether characteristic curves of the negative and the positive could be combined by this method to give a resultant linear curve, and whether the steps of such a process would be more or less critical than the steps of the positive printing process.

This was an entirely new approach to the problem of measuring X-ray intensities. No great guidance was obtained from chemical literature, and at first time was spent on experiments which were unnecessary, and on some which, in retrospect, were foolish. Nevertheless we did profit by our mistakes.

GENERAL BACKGROUND TO THE REVERSAL PROCESS

Using the multiple film technique, the writer estimated visually the intensities of the (hk0) zone of reflections in cupric tropolone. The structure factors derived from these intensities showed very poor agreement with those derived from intensities estimated visually by Professor Robertson[10]. Re-estimation of these intensities by the same method showed little improvement in agreement between the two sets of structure factors. It seemed desirable then to find a more objective method of measuring intensities.

During a discussion of the positive print method, Dr. G. Thomson, of this department, suggested that photographic reversal of the X-ray film might give a suitable positive image more readily than printing. Photographic reversal is used in processing amateur cine-films and it was thought that the high degree of contrast available there might well be obtained on a reversed X-ray film. Accordingly it was decided to examine the conditions necessary to produce a linear characteristic curve on a reversed X-ray step wedge.

The principle of photographic reversal is briefly as follows. The film is developed normally under a safelight. The silver so produced is then dissolved out of the emulsion by agitating the films in an oxidising bath consisting of potassium permanganate, ammonium persulphate, and sulfuric acid. During the oxidation-reduction process, lower oxides and hydroxides of manganese are produced and remain in the emulsion as a brown stain. These stains are removed by treatment with a solution of sodium metabisulfite, which reduces the Mn^{3+} and Mn^{4+} ions to the soluble Mn^{2+} ion. The silver halide left is then exposed to light, the films are developed again and fixed.

The parallel between printing and reversal is complete. These areas with a low silver concentration in the print have a low silver concentration in the reversed film. In the case of the print, such areas arise because a high silver concentration at the corresponding point in the negative prevents the printing light from activating so much silver halide as at other points. In the case of the reversed film, a high silver concentration produced during the first

development (corresponding to the negative) is dissolved out, leaving the area deficient in unactivated silver halide; when the film is exposed to light, and developed again, this area will have a lower silver concentration than its surroundings (corresponding to the positive).

The three critical steps in the Dawton technique have parallel steps in the reversal technique.

Positive print	Reversal
Development of negative	First development
Printing exposure	Exposure to light
Development of positive	Second development

In reversal the first development time should be controlled, but in fact it is so long that it is not critical.

The light exposure need not be controlled. It has been the practice during this work to expose the emulsion completely. This has been done by switching on the darkroom lights after the films have been placed in the oxidising bath. The remainder of the process is carried out under normal illumination.

The second development is critical, and time and temperature must be closely controlled. In the earlier work this was not fully realised.

EXPERIMENTAL WORK

I. - Controlled first development time

During the earlier part of this research no crystal photograph was processed. Attention was concentrated on processing step wedges, prepared on rotating sectors, and studying the characteristic curves obtained. The rotating sectors are described in a later section. The light exposure during processing was to infinity, the films being completely exposed by their prolonged exposure to the room lighting. The second development time was kept constant; in fact, when all the silver halide on the film had been activated, a development of 5 minutes, at 18°C was sufficient to develop the film completely, and no fixing was necessary.

Solutions used

In the first instance some guidance as to the concentration of the solutions to be used was obtained from the British Journal Photographic Almanac (1950). These were:

potassium permanganate	2 g./l.	(A)
ammonium persulfate	1 g./l.	(B)
sulfuric acid (conc.)	20ml./l.	(B)
sodium metabisulfite	40 g./l.	

The recommended oxidising bath consisted of equal volumes of solutions A and B mixed immediately before use.

In cinematographic work, a silver halide solvent is added to the developer used in the first development in order to reduce the density of the background, which might otherwise obscure some parts of the image produced by a low exposure. Accordingly, 9 g. potassium thiocyanate were added to each litre of Ilford ID-19 developer used in the first development. ID-19 alone was used in the second development.

Ilford 8B21 Recording Film

First attempts to reverse Ilford Industrial G X-ray Film were unsuccessful. The emulsion tended to strip off, and the background was far too black - the transmission through each step was zero. At that

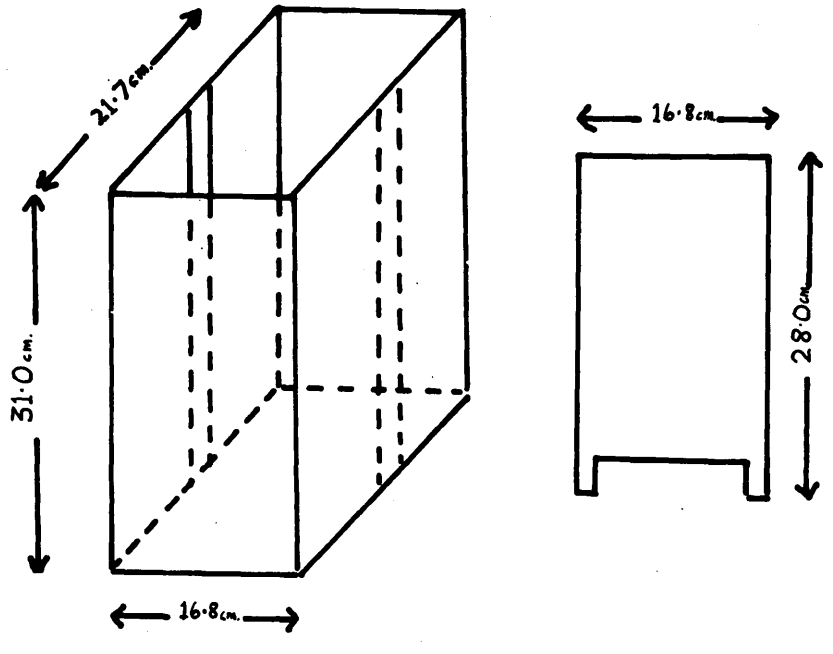


FIG. 5.

time it was uncertain whether a film with such a thick emulsion could be reversed. It was decided to try another film. Ilford 8B21 Recording Film was tried next. This film is a single coated film with a thinner emulsion than X-ray film. Taking these limitations into consideration it had a reasonably high speed to X-rays.

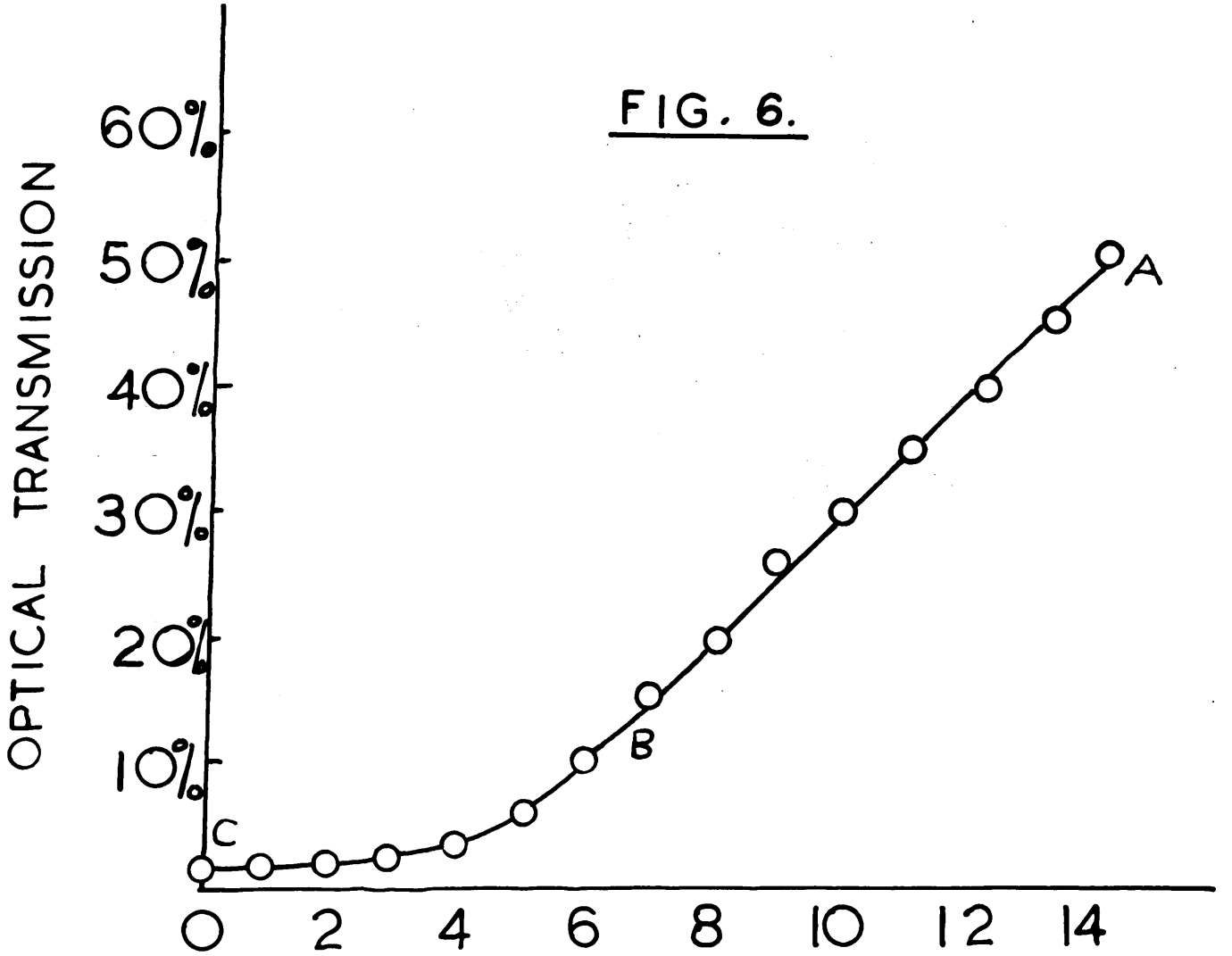
A qualitatively successful reversal was obtained using the solutions described above. However at the boundary between the wedge and the dense background (unexposed to X-rays) a black band was observed. This was thought to be an example of the Eberhard effect[11]. Where on a photographic film, a very dense area adjoins an area of low density, developer products tend to diffuse from the area of the emulsion with the high silver density into the area of low silver density. This causes an increase in photographic density at the junction. The effect is minimised by a rapid uniform flow of developer over the film. A developing tank to produce this effect was designed (Fig. 5).

The tank was constructed from sheets of "perspex", and had internal dimensions of 21.7 x 16.8 x 31 cm. A partition (28 x 16.8 cm.) was fitted inside, partially

dividing the tank in two. The tank was filled with developer. On one side of the partition was suspended the rack carrying the films. On the other side a mechanical stirrer was set in motion; the stirrer was made from a model ship's propellor, 2" in diameter. This pulled the developer up over the top of the partition, and down the other side, giving a rapid and uniform circulation of developer over the films.

Films developed in this tank showed no Eberhard effect, but it was difficult to obtain reproducible development. ID-19 developer contains a large proportion of sodium sulfite. In solution, sodium sulfite is rapidly oxidised to the sulfate by atmospheric oxygen. The presence of sodium sulfate reduces the activity of a developer[12]. Now as the developer circulated in the tank a new surface was continually being exposed to the atmosphere, and the sodium sulfite was given every opportunity to absorb oxygen. After one development the concentration of sodium sulfate in the developer was appreciable, and the activity of the developer was lowered; the presence of sulfate ions in the developer was shown by the barium chloride test.

FIG. 6.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RELATIVE X-RAY EXPOSURE.

This difficulty was minimized by using fresh developer each time, and by directing a stream of nitrogen over the surface of the circulating developer.

Even after these difficulties had been resolved, the experiments on 8B21 film were not completely successful. At 18°C 4 minutes 30 seconds was the optimum first development time, i.e. that development time which gives the characteristic curve with the widest linear range. This curve is shown in Fig. 6 AB is linear, but at the foot of the curve there is a non-linear portion, BC. This curve is then useless for X-ray intensity measurements.

B'C' on the negative curve (Fig. 2) represents the relationship between the images produced by a high X-ray exposure, and the optical transmission through them, i.e. the relationship between the optical transmission through areas of high density and the exposures producing them. This relationship is non-linear. Now on a reversed X-ray film, the areas of high density are those produced by a low X-ray exposure. Therefore, BC (Fig. 6) is identical with B'C' (Fig. 2), and if the characteristic curve is to be linear from the origin, then processing conditions must be adjusted

so that the origin lies at B (Fig. 6). In other words, the background in Fig. 6 is too dense, and its transmission must be increased until it reaches the value at B. This point has been discussed by Dawton in another way[9].

Theoretically, the background transmission can be adjusted in three ways:

a) By increasing the concentration of halide solvent in the first developer.

b) By introducing a controlled light exposure, instead of complete exposure, and fixing after development.

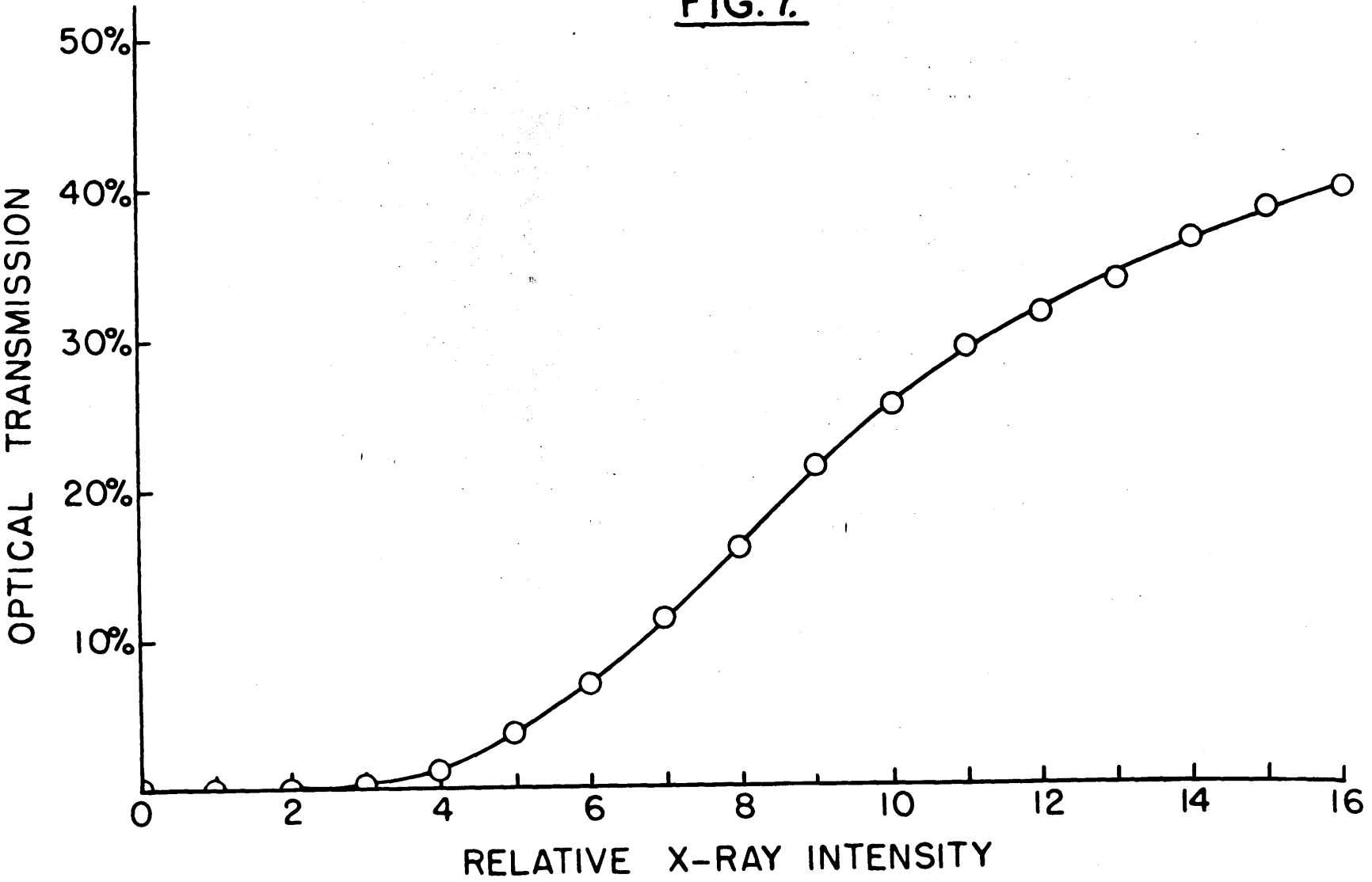
c) By introducing controlled second development, followed by fixing.

It seemed at the time desirable to concentrate on (a) since (b) and (c) introduced a second variable. At the same time it was felt that with the experience now gained it might be possible to reverse X-ray film. Accordingly, subsequent experiments were carried out on Ilford Industrial G X-ray Film.

Ilford Industrial G X-ray Film

This is a double coated film with two fairly thick layers of emulsion. To obtain the desired background

FIG. 7.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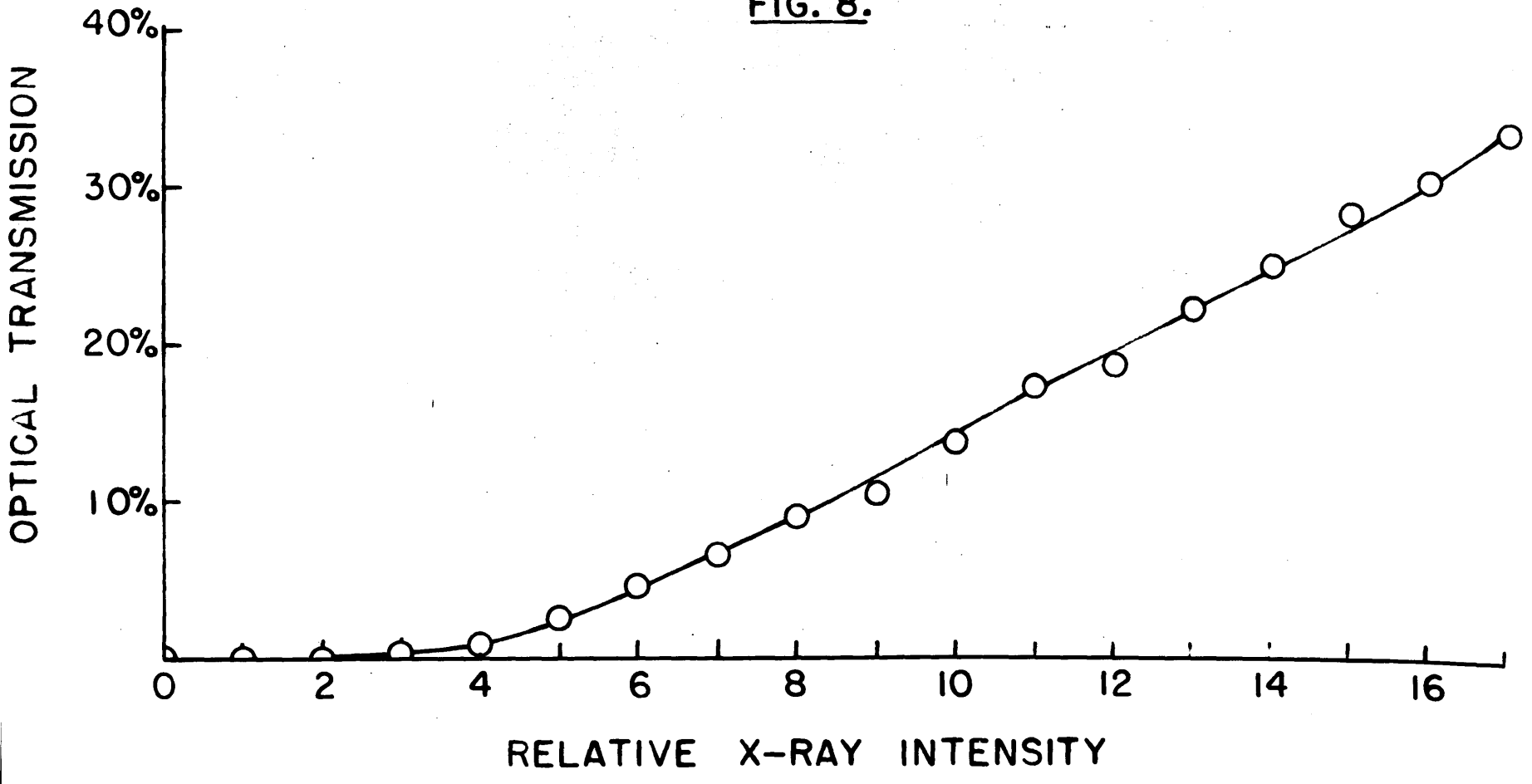
RELATIVE X-RAY INTENSITY

transmission, quite a lot of silver halide must be removed. It was decided to keep the halide solvent apart from the developer, to begin with at least. In this way the effect of a number of different halide solvent concentrations could be examined during the same experiment, meaning a great saving in time and materials. Sodium thiosulfate was used as halide solvent since potassium thiocyanate dissolves silver halides only when associated with developer. Sodium thiosulfate has the additional advantage of being more active.

While investigating the action of sodium thiosulfate on the X-ray film, the first development time was maintained at 4 minutes 30 seconds, at 18°C, with Ilford ID-19 developer. After the first development the films were treated with a solution of sodium thiosulfate at 18°C for 4 minutes 30 seconds. The remaining steps of the reversal process was as previously described. The concentration of the sodium thiosulfate was varied over a range from 2 grams per liter, to 10 grams per liter. The best characteristic curve was obtained using a concentration of 2 grams per liter, and is shown in Fig. 7.

FIG. 8.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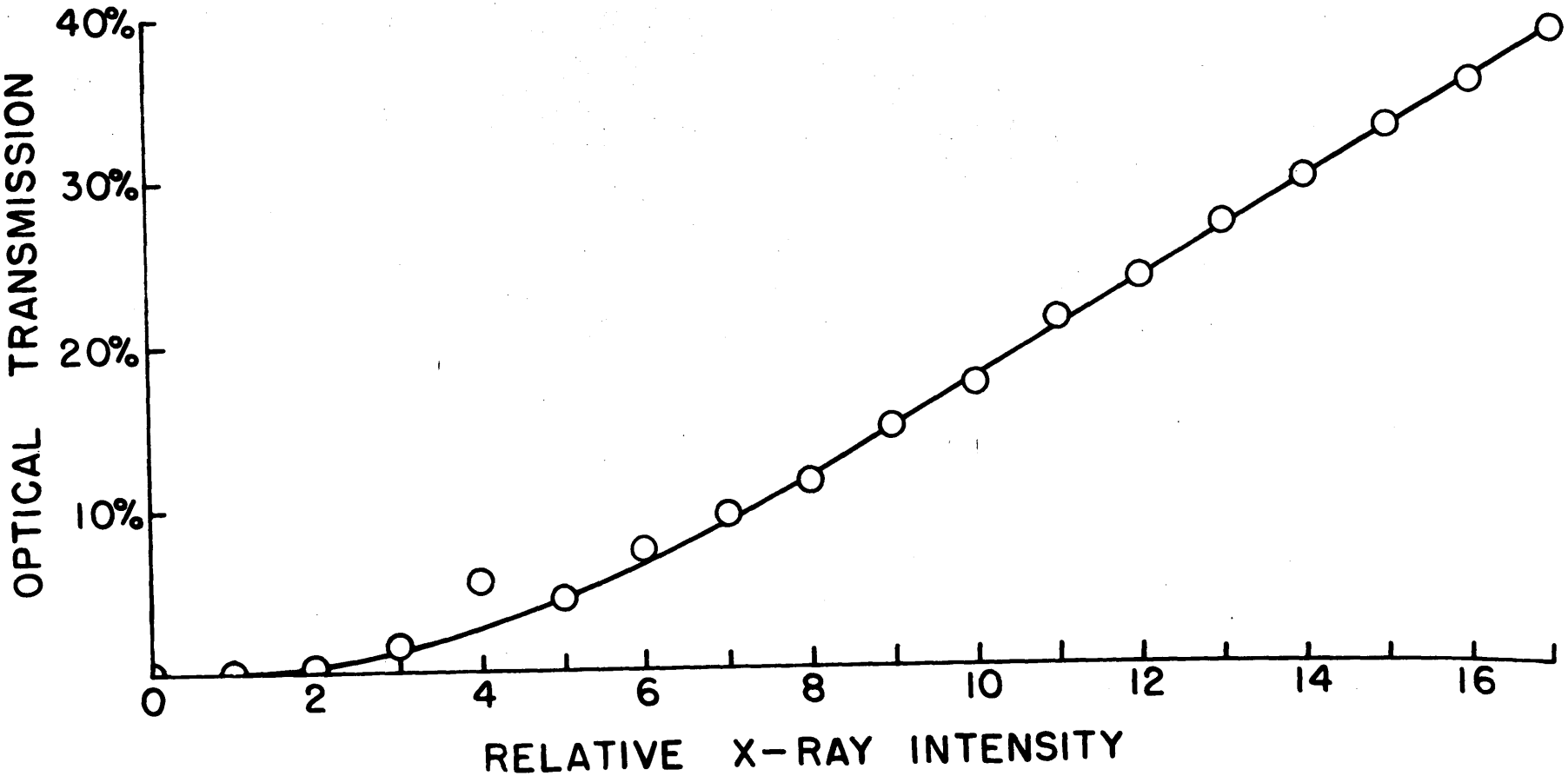
RELATIVE X-RAY INTENSITY

FIG. 9.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RELATIVE X-RAY INTENSITY

The concentration of sodium thiosulfate was then maintained at 2 grams per liter and the time of treatment varied. It was found that 2 minutes 30 seconds treatment with this solution gave a reversed film with a slightly better characteristic curve (Fig.8).

This was the best curve that could be obtained using thiosulfate as the halide solvent. Concentrations below 2 grams per liter gave curves with a wider non-linear range. Higher concentrations and longer times of treatment tended to produce an uneven result. However it was decided to try the effect of a prolonged first development. A step wedge exposed on X-ray film was developed for 18 minutes at 18°C, treated for 2 minutes 30 seconds in the sodium thiosulfate solution (2 g./l.) at 18°C, and reversed as before. The characteristic curve measured from this film is shown in Fig. 9. There is a slight improvement over that in Fig. 8, but non-linearity persists in the region of low X-ray exposure.

It was obvious by this time that it would be very difficult to obtain a linear characteristic curve for X-ray film simply by manipulating the first development time. Still we were unwilling to introduce the

complication of a controlled light exposure or controlled second development if it could possibly be avoided.

Ilford Fast Blue-Sensitive X-ray Film

Some Ilford Fast Blue-Sensitive X-ray film was then acquired. This is a single-coated film with a speed only slightly less than that of Ilford Industrial G X-ray Film.

This film gave a qualitative reversal without treatment with halide solvent. Another important property of this film was that it showed no Eberhard effect. It was possible then to dispense with the developing tank described previously. This meant that much less developer was used at one time, but for safety the developer was still used only once.

At this point a further complication arose. The emulsion of the Fast Blue-Sensitive Film swelled during processing. The steps on the wedges were so reticulated that it was impossible to measure their transmissions with accuracy. It was observed that a reduction of the concentration of sulfuric acid reduced the swelling to some extent. Also, where the film had been given prolonged treatment in the oxidising bath,

i.e. where the film was in contact with the sulfuric acid for a longer period, the swelling was worse. It was reasonable to conclude that the sulfuric acid was reacting with the emulsion in some way. When the concentration of sulfuric acid in the oxidising bath was reduced, the swelling subsided to some extent.

Further attempts to cut out this swelling followed well established photographic lines. The temperature of all solutions, including the washing water, was fixed at 18°C, and more thorough washing was introduced between each stage. Sodium sulfate was added to the developer as a hardener in a concentration of 45 grams per liter. These measures produced an improvement in the state of the finished wedges which was considered adequate until the time came to process multiple film series, when a further improvement was necessary.

The effect of varying the first development time with Fast Blue-Sensitive Film was systematically investigated using the following process.

Solutions used

Ilford ID-19 developer with 45 g./l. sodium sulfate heptahydrate

Potassium permanganate	: 4 g./l.	(A)
Ammonium persulfate Sulfuric acid (conc.)	: 0.25 g./l.) : 5 ml./l.)	(B)

Equal volumes A and B mixed immediately before use.

Sodium metabisulfite : 40 g./l.

Conditions

First development	Time varied
Washing	8 minutes
Bleaching	7-10 minutes
Washing	5 minutes
Clearing	1-2 minutes
Washing	5 minutes
Second development	7 minutes
Final washing	5 minutes

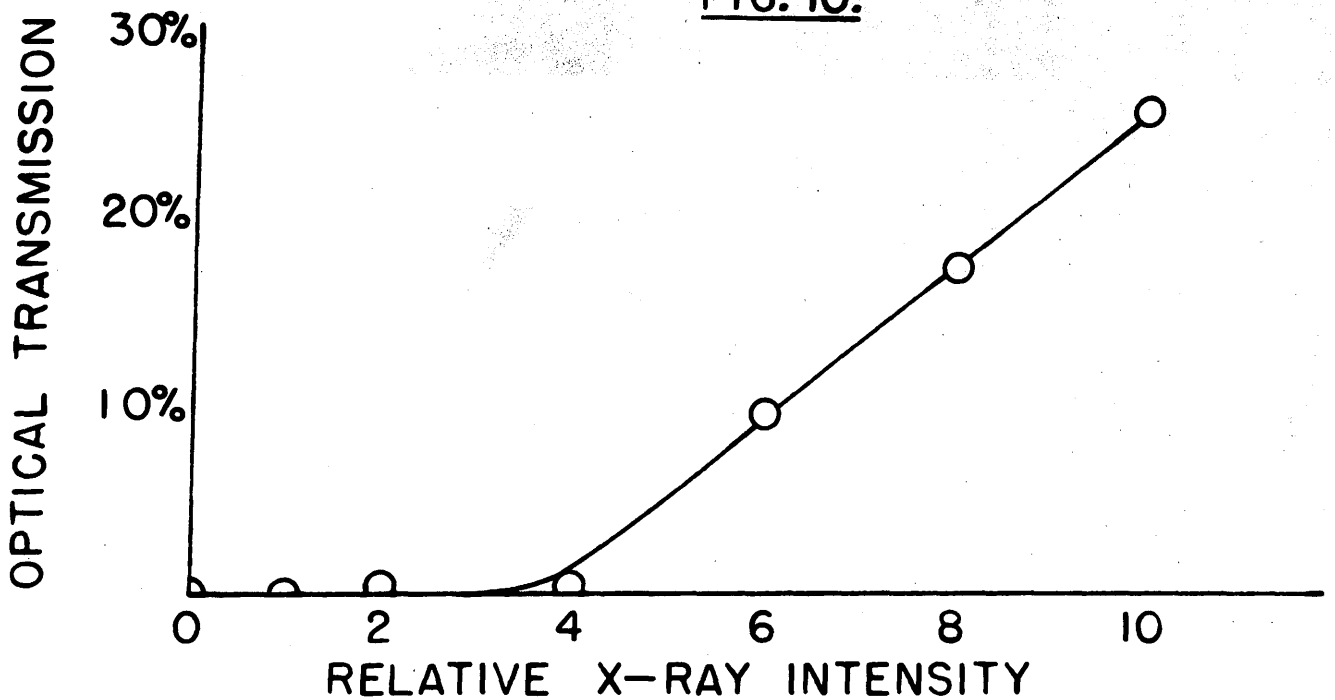
The temperature of all solutions was maintained at 18°C. The main darkroom lighting was switched on just after the films were placed in the oxidising bath.

The first development time was varied over the range 3.5 minutes to 23 minutes, in the following way.

3.5 minutes to 7 minutes by intervals of 0.5 minutes

7 minutes to 23 minutes by intervals of 2 minutes.

FIG. 10.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RELATIVE X-RAY INTENSITY

The most promising characteristic curve was given by a first development time of 23 minutes. This curve did not differ significantly from that obtained by the first development time of 21 minutes. It was felt that a limit had been reached, and that extension of the first development time beyond 23 minutes would be of no advantage. The curves are shown in Fig. 10.

It will be observed that the 23 minutes curve is not linear to the origin. The non-linear portion is considerably shorter than in Figs. 6-9. Even so, it is clear that, using these conditions, useful information about the intensities of X-ray reflections is unobtainable. It was not possible to find conditions which would give a linear characteristic curve by adjusting the first development time alone.

II Controlled First and Second Development Times

After failing to produce a linear characteristic curve by varying the first development time, it was necessary to investigate the effect of controlling either the light exposure or the second development time. Ilford Fast Blue-Sensitive Film was retained as the experimental film.

Some preliminary experiments were carried out on control of the light exposure. Apart from the light exposure, the conditions used were those which gave rise to the characteristic curve shown in Fig. 10. The entire process was of course carried out under the dark-room safelight. The films were given varying exposures to light immediately before the second development. The light source was a 250 volt/15 watt clear glass tungsten filament bulb at a distance of 6 feet 0 inches from the films. When a wet film is exposed, little droplets of water on the surface can act as lenses, and can concentrate light at particular points, giving an uneven exposure. To avoid this effect, the films were exposed under water in a developing tray; the water depth above the films was 0.5 inch. Different films were given exposures of 1,2,4,8,16 and 32 seconds under these conditions.

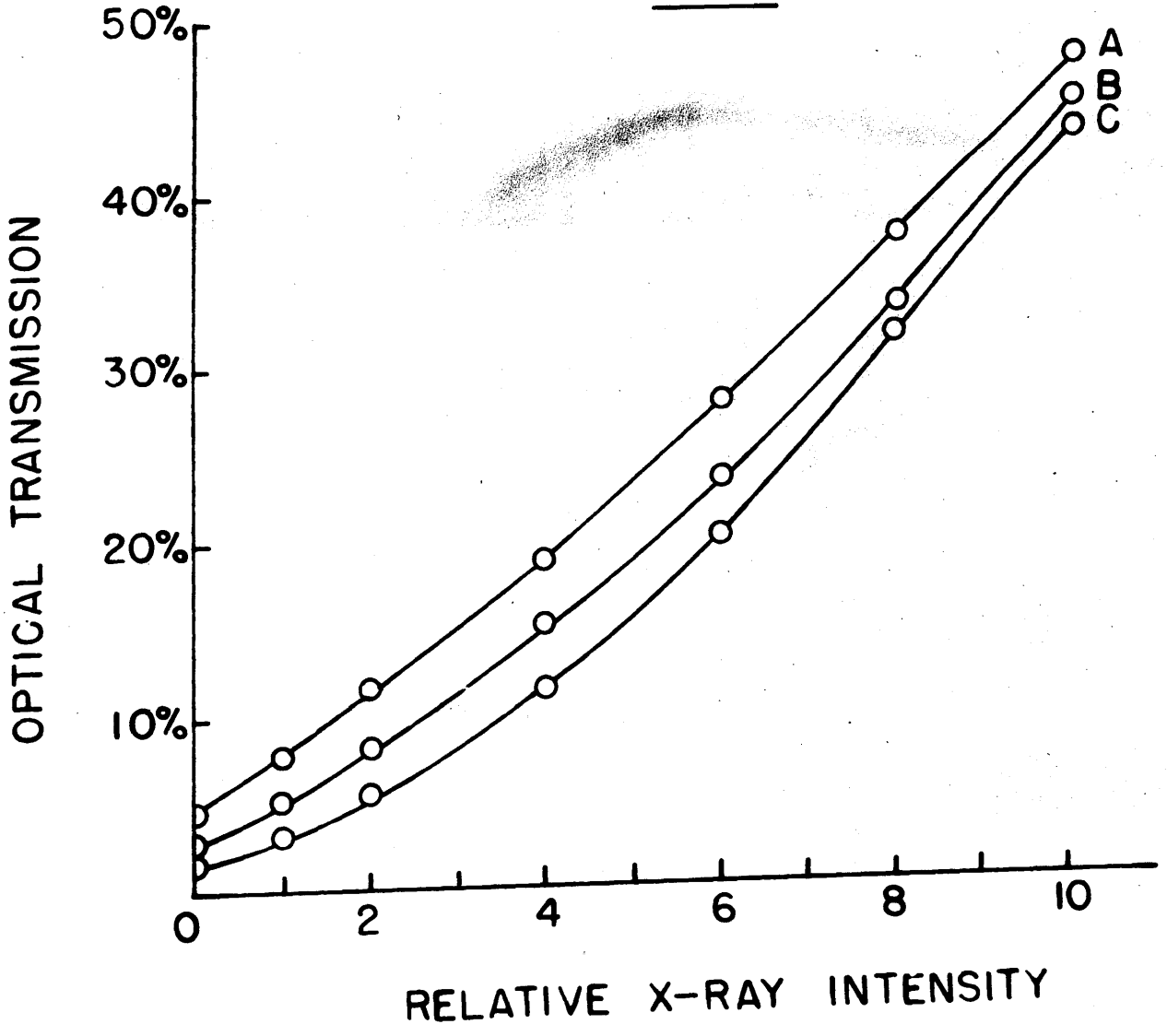
These experiments were unsuccessful. Light passed through the steps of the wedge and was reflected back from the bottom of the tray. On subsequent development, this caused a black "halo" to appear around each step. Thus the areas immediately surrounding the steps were

overexposed with respect to their neighboring areas. Using a flat-black dish made no difference. It seemed that the wet surface of the dish too easily reflected the light transmitted by the steps. The only obvious ways to overcome this were either to expose to X-rays, or to dry the films before exposure to light. Either alternative seemed an unfortunate complication. Also, with regard to an exposure to X-rays in particular, it is difficult to specify exposure conditions in such a way that the identical exposure may be given in another laboratory with different apparatus. It was decided to discontinue the investigation of a controlled light exposure, for the time being at any rate.

Control of second development

It soon became apparent that the second development time would have to be very short. In the first experiment, four step wedges were given a first development time of 23 minutes and a second development time of 2,3,4,5 minutes respectively in the ID-19 - sodium sulfate developer at 18°C. (After the second development, they were treated for 5 minutes in a solution of Ilford IF-9 quick fixing salt. In other respects,

FIG. 11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RELATIVE X-RAY INTENSITY

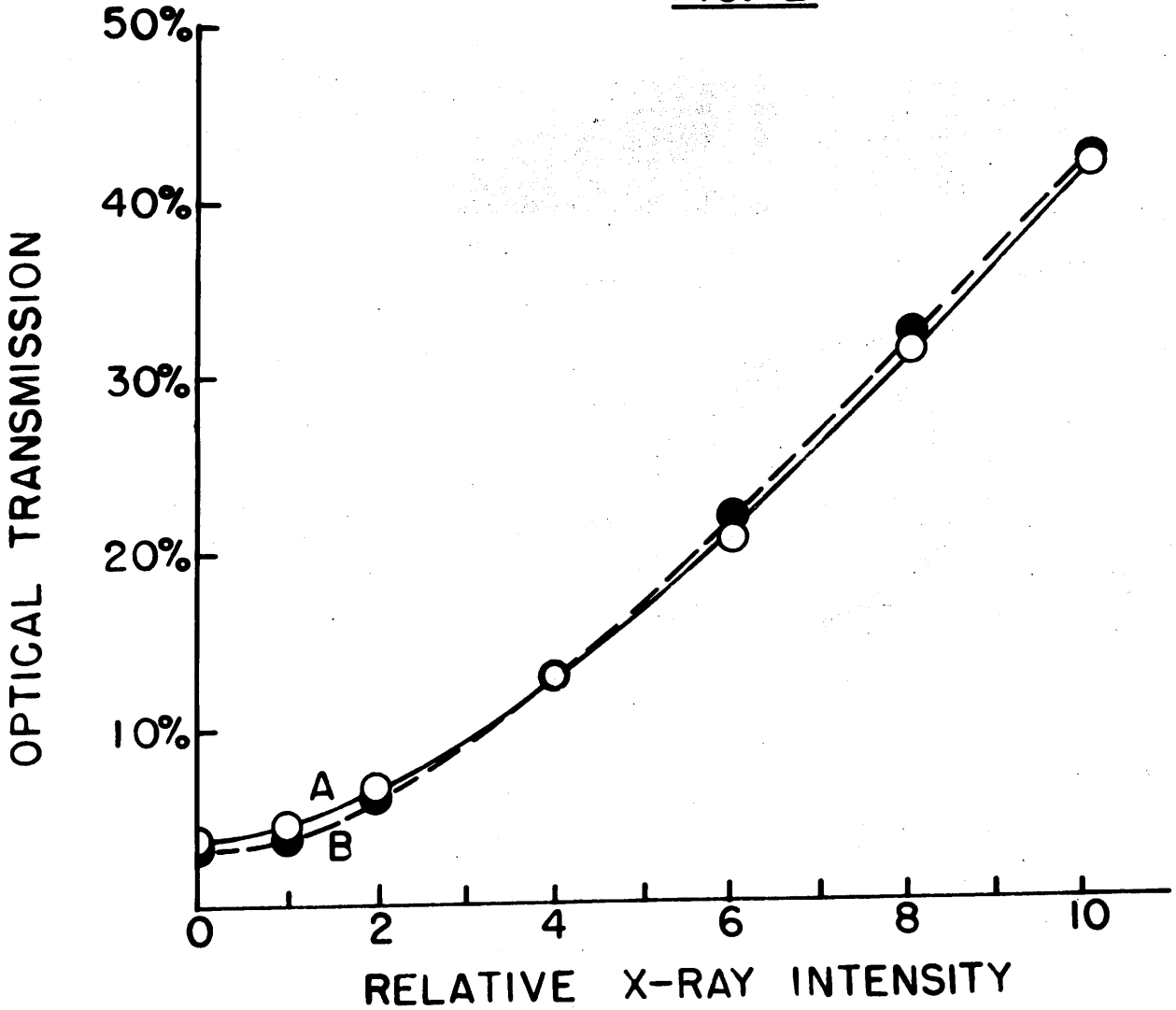
the process was identical with that described on page 22.) The characteristic curves of all were far from linear. Times of less than two minutes were difficult to measure accurately, and uneven development was produced.

It was necessary then to find some developer which was less active than ID-19, giving a longer and more easily controlled development time. Then the first development could be carried out in ID-19 with hardener, and this new developer used for the second.

The first such developer tried was a 25% solution of ID-19. It was made up by diluting one volume of ID-19 solution with three volumes of water. Three films were processed together and given second development times of 1 minute forty-five seconds, 2 minutes, and 2 minutes 15 seconds in 25% ID-19 at 18°C. The characteristic curves of these films are shown in Fig. 11. A second development time of 2 minutes gave a product with characteristic curve linear to the origin. This was a most encouraging result, and it indicated that it was possible to obtain a film with a linear characteristic curve by means of reversal.

At this point it was felt desirable to make further efforts to control the swelling of the emulsion (page 21). Adding sodium sulfate to the developer had not suppressed the effect completely. Other hardeners had not been previously tried since none could be used in any of the processing solutions; to use them meant introducing another stage into the process. However, there was no alternative now. Immediately before the second development some films were treated with chrome alum acid-hardener, but this made the swelling worse. This should perhaps have been anticipated since the swelling had been connected up with the sulfuric acid in the oxidising bath. Acid hardeners being useless, formalin was tried. It was found that the swelling was completely inhibited by treating the films for 15 minutes in a 5% solution of formaldehyde, immediately before the second development. Using a formaldehyde bath, it was no longer necessary to add sodium sulfate to the developer, but the temperature of all solutions was rigidly maintained at 18°C, and the revised washing times retained (page 22).

FIG. 12.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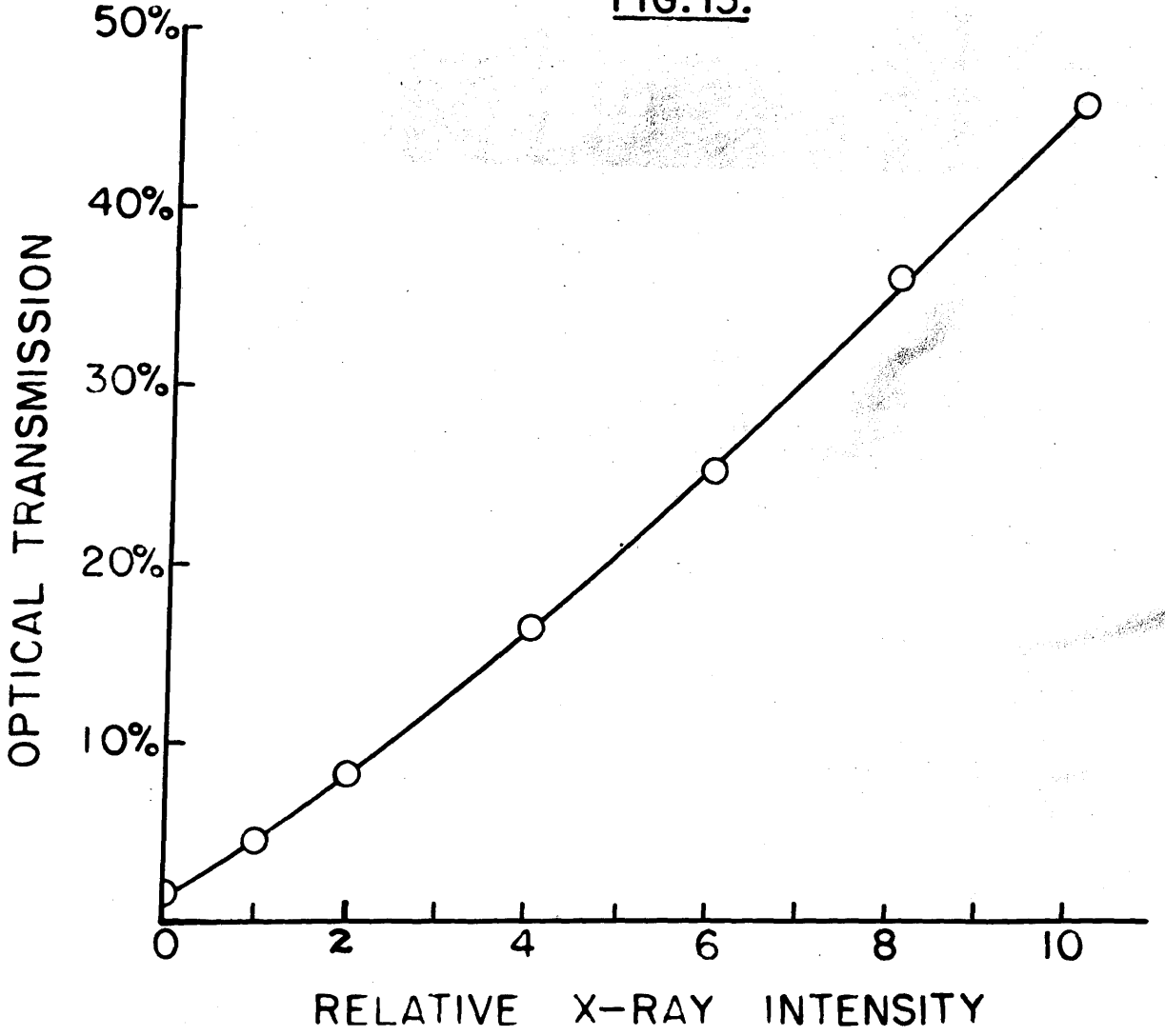
RELATIVE X-RAY INTENSITY

Refinement of conditions for the second development

A second development time of 2 minutes, was too difficult to control in practice. An error if five seconds would impair the linearity of the characteristic curve of the film. In an effort to prolong the second development it was decided to use a 5% solution of ID-19 developer i.e., one volume of ID-19 solution diluted with nineteen volumes of water. Two films were processed with second development times of 6 and 7 minutes, respectively, and with the other conditions the same as described in the previous section. The characteristic curves of these films are shown in Fig. 12. These are linear to the origin except for the bottom step of the wedge. This means that the regions of higher silver halide concentration are being over developed with respect to the others. This would suggest that the low silver halide concentration on the upper steps, and the exceedingly low developer concentration combined to make the development process relatively inefficient on the upper steps.

Now, the activity depends both on the concentration of the developing agent, and on the pH of the solution.

FIG. 13.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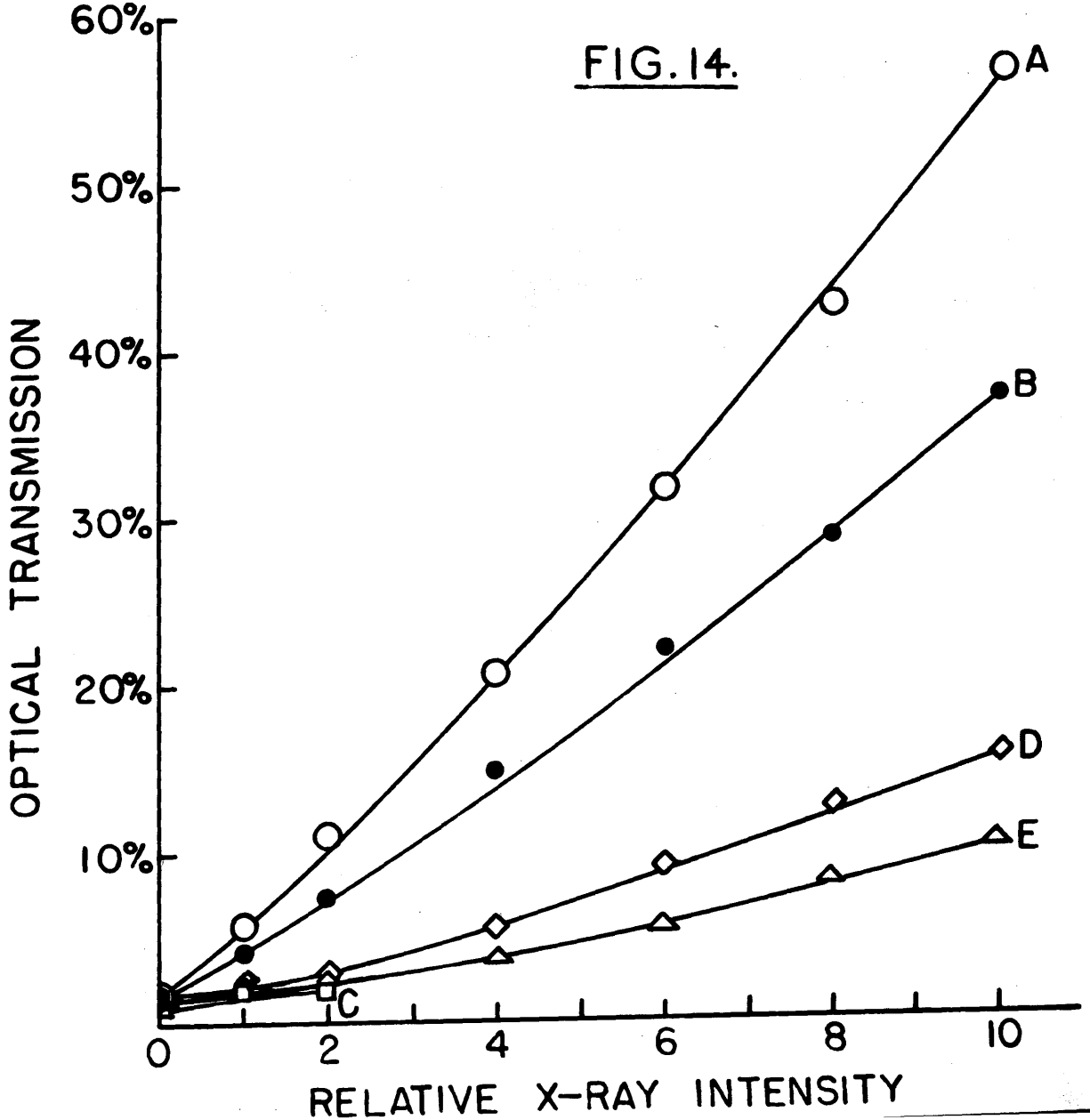
RELATIVE X-RAY INTENSITY

It was decided to try the effect of using a "compromise" developer. In this developer the concentration of "Metol" and hydroquinone was that of 25% ID-19, and the concentration of sodium carbonate was that of 5% ID-19. In this way it was hoped to preserve the efficiency of development of 25% ID-19 by the higher concentration of developing agents, and at the same time prolong the development time by reducing the sodium carbonate concentration. This developer will be referred to as RD.

This developer proved very successful. A step wedge was processed with a second development time of 4 minutes 15 seconds in RD at 18°C. The characteristic curve is linear from the origin, and is shown in Fig. 13. It is seen that this development time is intermediate between 2 minutes, obtained with 25% ID-19, and 6-7 minutes, with 5% ID-19.

The effect of varying this time of 4 minutes 15 seconds, was then examined. Packs of five films were made up. Each film was separated from the next by two thicknesses of black paper. Care was taken that the emulsion of each film was facing the same way. Four such packs were exposed in the rotating

FIG. 14.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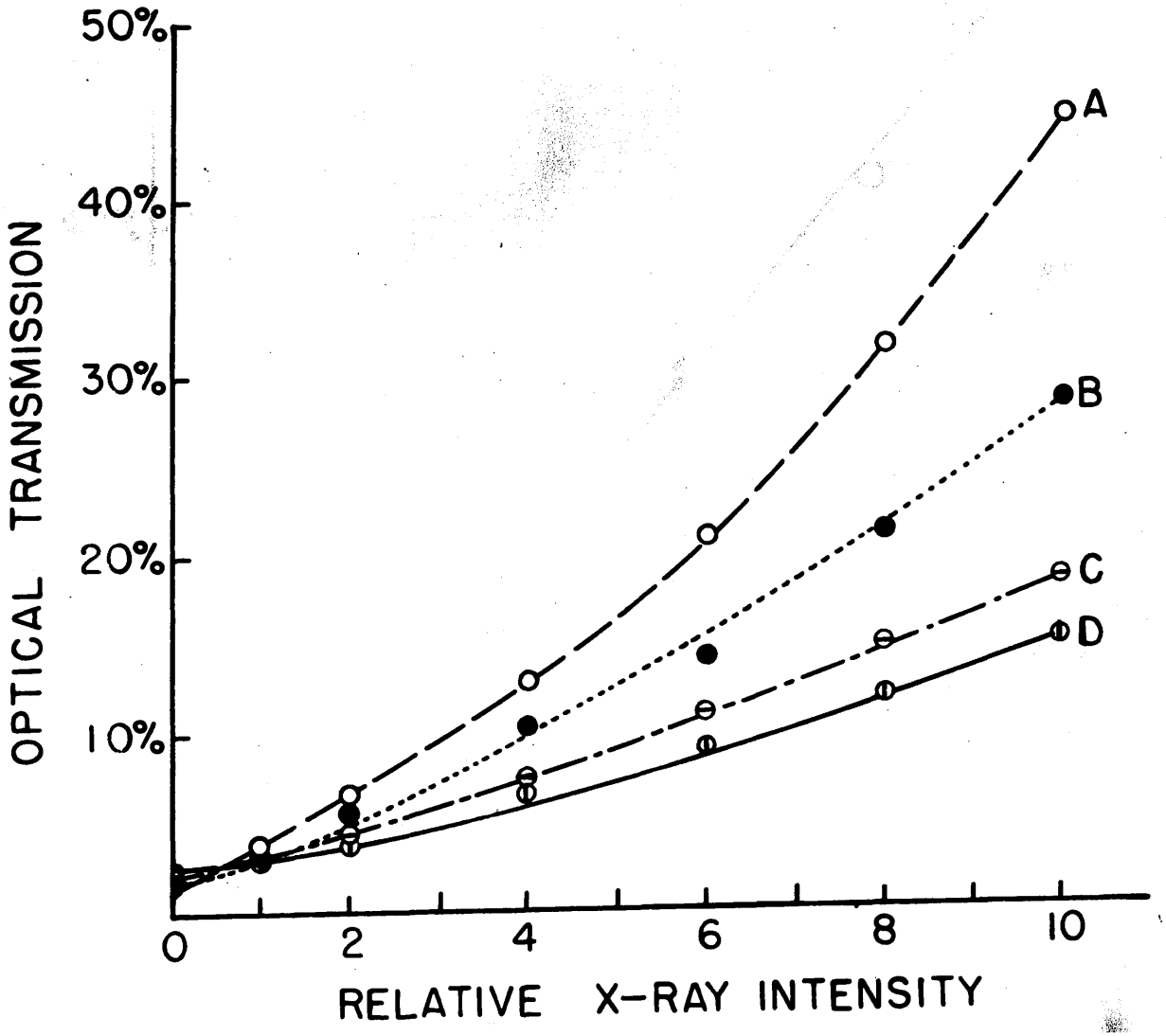
RELATIVE X-RAY INTENSITY

FIG. 15.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RELATIVE X-RAY INTENSITY

FIG. 16.

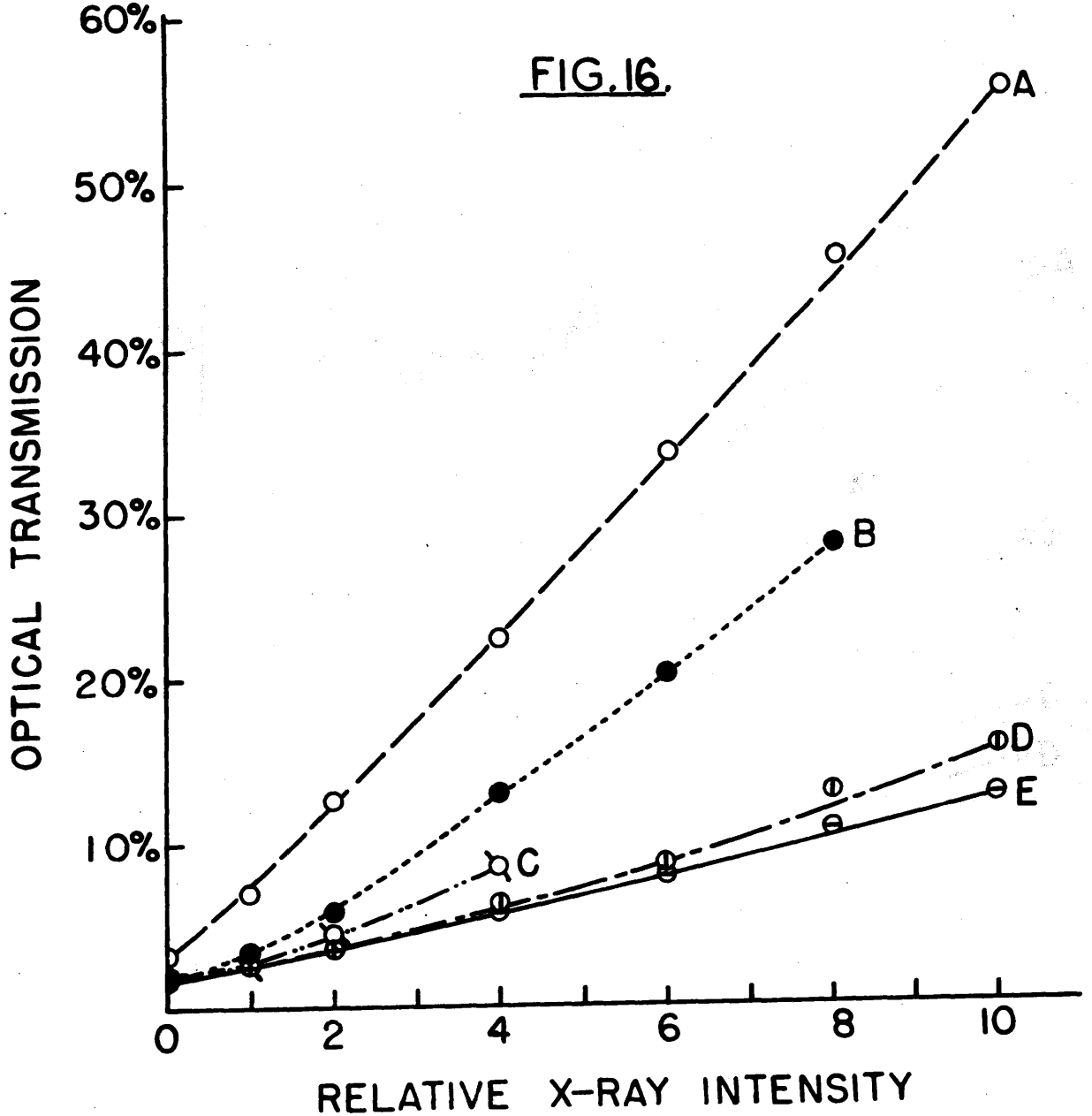
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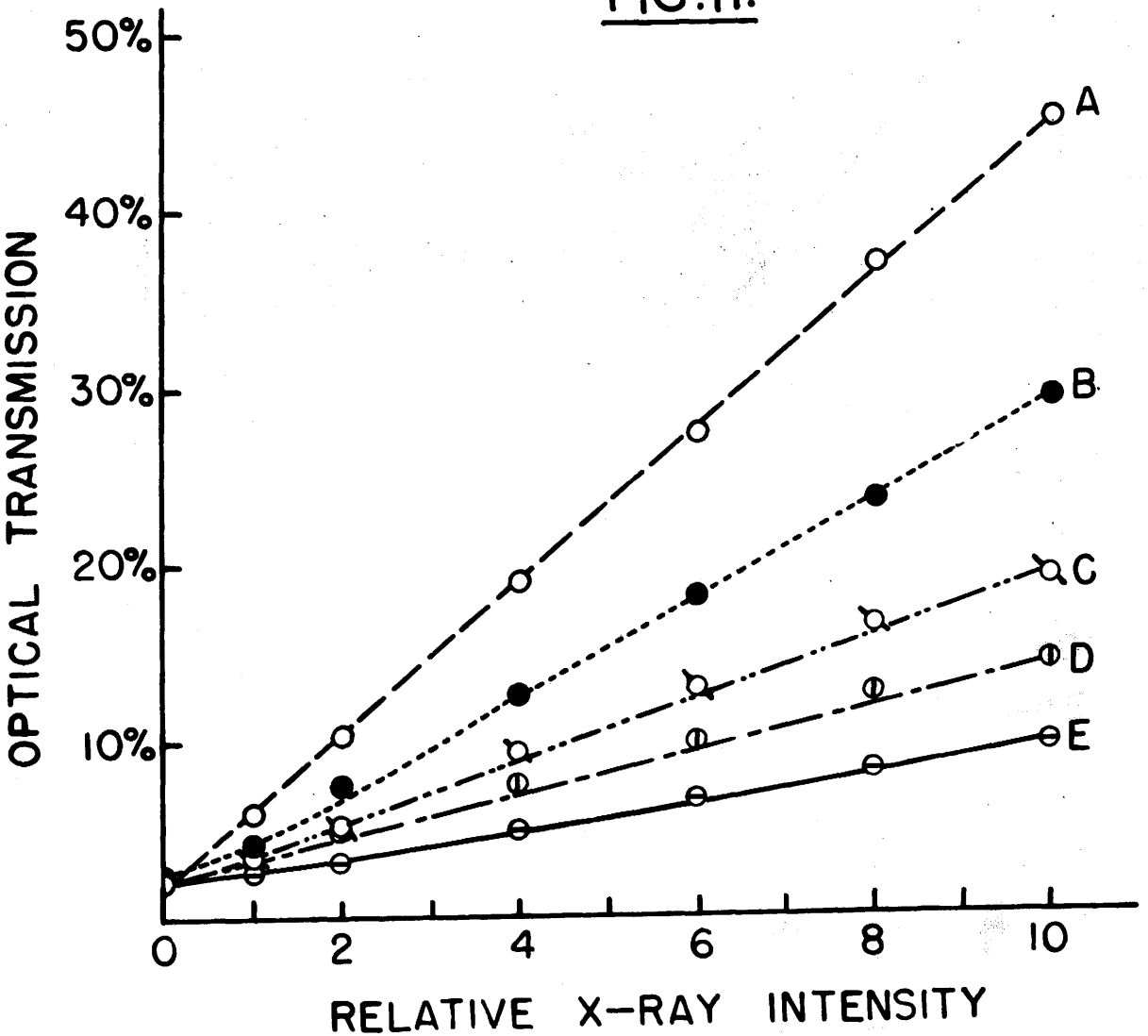
FIG. 17.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RELATIVE X-RAY INTENSITY

sector. They were processed with second development times of 4 minutes, 4 minutes 10 seconds, 4 minutes 20 seconds and 4 minutes 30 seconds respectively. The characteristic curves of each film in a pack were plotted together. The plots for all four packs are shown in Figs. 14-17.

Thus a second development time of between 4 minutes 30 seconds gives a linear characteristic curve on all five films. This means that on a series of five films the relationship between the X-ray exposure and the transmission of the reflections is linear on all five films.

Kodak Medical X-ray Film

The work done on Kodak Medical X-ray film was carried out at Brown University, U.S.A. This film is very similar to Ilford Industrial G X-ray films, and is generally used in X-ray crystallographic work in the U.S.A. Using this film, the solvent action of sodium thiosulfate on the silver halide was studied over a range of sodium thiosulfate concentrations. Also pieces of film were exposed for different times to sodium thiosulfate solutions of the same concentration.

All of these experiments were repeated using different forms of agitation, including no agitation at all.

The object of these experiments was to try to find conditions under which the quantity of silver halide, necessary for satisfactory reversal of the film, could be uniformly removed. It was hoped that the successful sodium thiosulfate solution could be combined with the first developer. This would mean that the second development would not be critical. Also, if the sodium thiosulfate solution were fairly dilute, it would not be necessary to control the first development too closely.

However a suitable solution was not found.

The concentration of sodium thiosulfate was veried between 1 g. and 64 g., doubling the concentration at each experiment, e.g. 1 g., 2 g., 4 g., 8 g., etc. The best result was obtained using a solution of 25 g. sodium thiosulfate per liter, and giving the film 15 minutes in the solution at 30°C with regular agitation by hand. The film was then exposed and developed completely. Even this was far from being useful. The silver halide had been removed in a

rather patchy manner. The film contained areas of high and low density haphazardly distributed. In addition all the silver halide had been removed at the edges, and at other points where the film touched the supporting steel frame. This procedure was repeated several times to try to improve the result, but without success.

The same deficiencies were present to a greater degree in the other solutions tried, no matter what type of agitation was employed. In one set of experiments no agitation was used. In others, various modes of hand agitation were tried. Finally the sodium thiosulfate solution was circulated mechanically over stationary films.

There would appear to be little possibility at present of using a halide solvent in the first developer.

PROCESSING APPARATUS

Rotating Sectors

Two rotating sectors were used. For the experiments with Ilford 8B21 Recording Film and Ilford Industrial G X-ray Film the rotating sector used was manufactured by Unicam Instruments (Cambridge) Ltd. The sector exposed eighteen steps, 3.5 mm X 4.0 mm, with exposures related in the ratio 1:2:3: ..... :18. The motor rotating the sector was guaranteed to operate at 2,500 r.p.m. The ratio of the radius of the motor wheel to that of the sector driving wheel was 1:4 and so the maximum speed of the sector was about 600 r.p.m.

The "Unicam" rotating sector is designed to expose films with a maximum width of 2.5 cm., and is therefore unsuitable for superimposing step wedges on crystal photographs. The step wedges exposed on Ilford Fast Blue-Sensitive Film were made on a rotating sector built in this department. This sector could accommodate all sizes of film normally used in crystallographic work. It gave six circular steps of diameter 1.5 m.m., with exposures related in the ratio 1:2:4:6:8:10. The sector was driven by the motor from the "Unicam" rotating sector. The ratio

of the radius of the motor wheel to the sector driving wheel was 2:1. and so the maximum speed of the sector was 5,000 r.p.m.

Exposures were made in the center of the X-ray beam at a distance of 2 meters from the window of the tube in order to ensure that the beam falling on the sector was of uniform intensity. For 8B21 film an exposure of 200 seconds was required to give steps with transmission ranging up to 100%. With Industrial G X-ray Film an exposure of 80 seconds was adequate, and with Fast Blue-Sensitive Film, 60 seconds.

A sealed type X-ray tube, operating at 10 milliamperes filament current, was usedas the source of radiation.

Processing frames and racks

When exposing step wedges it was unnecessary to use full sized film. Strips of film were cut measuring 2 1/4" x 1". For processing these strips were fitted into the lower part of frames measuring 2 1/4" x 3 1/4". The frames themselves were then fitted into a rack which could accommodate four frames at once. In this way it was possible to process four strips simultaneously, giving them identical

processing conditions. When investigating the effect of different developing times, a frame could be removed from the rack when its film had had the required time in the developer; in this way four different development times could be investigated during one reversal process. Each frame was numbered in order to differentiate between films after processing.

When it was found that Ilford Fast Blue-Sensitive X-ray Film showed no Eberhard effect it was possible to dispense with the partitioned development tank (p. 14) and the films were processed in one liter beakers. This was far more economical.

Ilford Fast Blue-Sensitive Film is supplied in one size only, 4" x 5". When crystal photographs were taken, packs containing five of these films were exposed as a "Unicam" Weissenberg Spectromoter (camera radius, 3 cm., and length of travel, 10 cm.). (Unfortunately, the film is too small to be used in a Weissenberg spectrometer with larger radius or longer travel). These five films were processed together in Ilford 4" x 5" developing frames supported in an Ilford adjustable rack (Ilford Processing Rack, No. 1).

Processing tanks

In the final stages of the experimental work, all the steps in the processing were carried out in 2.8 l. tanks, with the exception of the second development and washing. These tanks were the Ilford No. 1 Processing Tanks.

The second development was carried out in the tank already described (p. 14) with the stirrer and the partition removed. 10.1 of developer were used.

The films were washed in a large tank of 15 l., capacity. The tank drained from the bottom through a siphon. This is the most efficient type of washing tank since developer products tend to sink to the bottom of the tank and so are removed most quickly by siphoning. Excess water not removed by the siphon flowed out from the top through an overflow pipe.

PROCESSING SOLUTIONS

Concentration of solutions

The solutions described in this section, and their concentrations, are those used in the final part of this work to process crystal photographs.

First developer

Ilford ID-19 developer was used in the concentration as supplied. Normally 4.5 l. were made up at one time. This was sufficient for two reversals.

Bleaching Solution

A Potassium permanganate 4 g./l

B Ammonium persulfate 0.5 g.)
Concentrated sulfuric acid 5 ml.) per 1.

The ammonium persulfate and sulfuric acid were dissolved in the same solution, B. For bleaching, equal volumes of A and B were mixed immediately before use. After use the solution contains a brown sludge consisting of the lower oxides and hydroxides of manganese; as a result the solution was discarded after use.

Clearing solution

Sodium metabisulfite 40 g./l.

This solution could be used several times.

Formaldehyde hardener

100 ml. 40% solution made up to one liter with water. This solution could be used several times.

Second developer

Metol	11 g.
Hydroquinone	45 g.
Sodium sulfite heptahydrate	780 g.
Potassium bromide	28 g.
Sodium carbonate (anhydrous)	42 g.
Water to make up to 5 l. solution	

Dissolve chemicals in the order given. For use dilute one volume of this developer with three of water.

Acid fixer

Ilford IF-9 fixer was used in the concentration supplied.

Notes on preparation of solutions

Developers

Since large quantities of developer were being used throughout this research, it became desirable to find a rapid way of making up developer solution.

It is not a good practise to heat developer, and so hot water could not be used to hasten solution of the chemicals; the developing agent will oxidise very readily in hot solution, especially before the sodium sulfite can be added to protect it.

The developers were finally made up with the aid of a chromium plated brass mechanical stirrer. When operating at high speed the stirrer hastened the solution of the chemicals in such a way that the ID-19 and RD developers could be made up in about 5 minutes.

However there is one serious danger encountered in using a high-speed stirrer. Violent stirring causes fresh developer surfaces continually to be exposed to the atmosphere. This encourages air oxidation of the sodium sulfite in the developer to sodium sulfate. The presence of sodium sulfate in the developer reduces its activity[12]. This same difficulty was encountered at first with the partitioned developing tank (p. 15).

In order to eliminate uncertainty in the activity of the developers it was necessary to prevent contact between the developer surface and the atmosphere while

the stirrer was in operation. This was achieved by directing a stream of oxygen-free nitrogen into the vortex, and also over the surface of the solution.

Ammonium persulfate - sulfuric acid solution

When solid ammonium persulfate and concentrated sulfuric acid are allowed to come in contact, they react with explosive violence. The reaction probably consists of oxidation of the ammonium ion to free nitrogen. Precautions were taken to avoid an explosion when the solution was made up. The two reagents were dissolved separately at first, using as much water as possible. The two dilute solutions were then mixed with constant stirring.

FINAL PROCESSING CONDITIONS

The following is a statement of the final conditions under which the films were produced which have the characteristic curves shown in Figs. 14 to 17. These conditions were used to process the final crystal photographs also.

First development	23 minutes ± 1 with gentle regular agitation
Washing[a]	8 minutes ± 2
Bleaching	10 minutes ± 2, with violent agitation
Washing[a]	5 minutes ± 1
Clearing	1 - 2 minutes
Washing[a]	5 minutes ± 1
Formaldehyde hardener	15 minutes ± 2
Washing[a]	5 minutes ± 1
Second development[b]	4 minutes 15 seconds, ~~15 seconds~~, with vigorous agitation
Rinse in water[c]	10 seconds - no longer
Fixing	10 minutes ± 2
Final washing[a]	4 - 5 minutes

Notes

The temperature of all solutions, except developers, and including washing water, should be maintained at 18° C ± 2° : the developer solutions should be maintained at 18.0° C ± 0.2°.

a) Washing times given are those found experimentally to give the most satisfactory reversed film.

b) In the second development the character of the agitation is important. The films should be agitated in a circular movement in a vertical plane. The ideal agitation consists of a fixed number of movements in a counter clockwise direction, then the same number of movements in the clockwise direction, and so on. This is necessary, since development is being interrupted. If agitation consists of movement up and down the direction of a straight line, striations will be observed on the reversed film i.e. alternate regions of low and high photographic density due to non-uniform development.

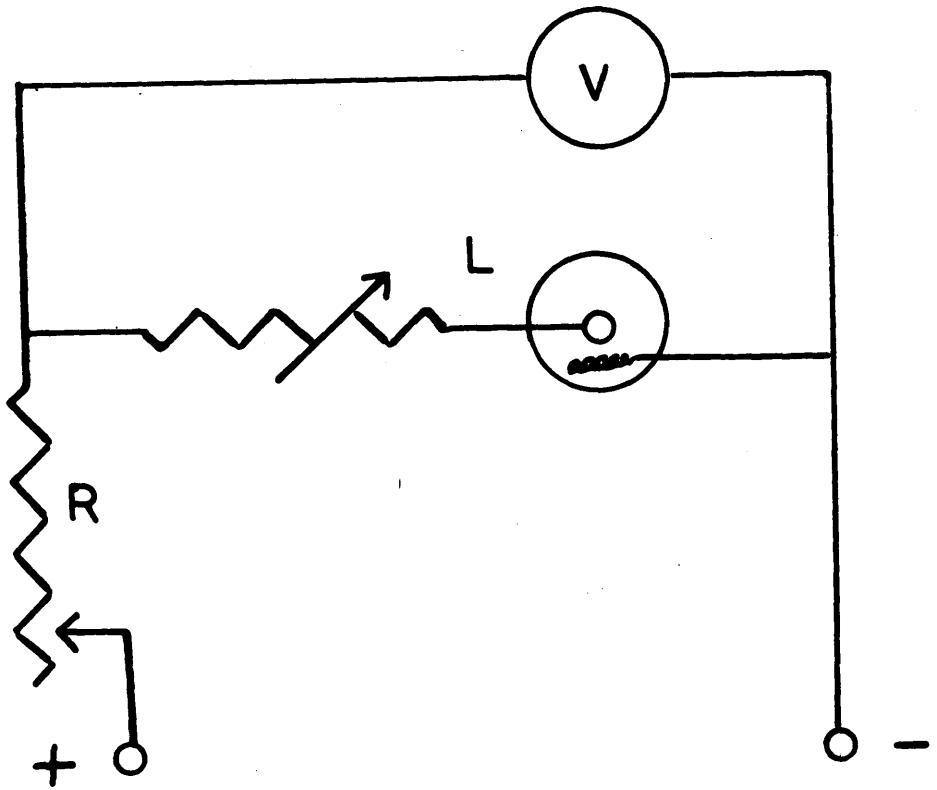
c) If, after the second development, the films were soaked in water for much longer then 10 seconds, the emulsion began to swell, i.e. the effect described on page 21 reappeared. It was found better simply to dip the films three or four times in clean water, and transfer them rapidly to the fixing bath.

PHOTOMETER

The photometer required for measuring the intensities of X-ray crystal reflections on reversed films is one which can measure instantaneously the light transmitted from a beam large enough to include any reflections on the film. A scanning photometer is unnecessary, and a microphotometer is useless. All that is needed, in principle, is a light beam of 1 to 2 m.m., in diameter and of uniform intensity, and a photocell to record the transmitted light.

Such a combination was not available in this department. Fortunately it was possible to borrow a photometer from the University of South Wales at Cardiff. This photometer was designed for use with the positive print method, and has been described elsewhere[13]. For the Weston Type I Phototronic selenium barrier photocell was substituted a Weston Type II Phototronic cell equipped with a "Viscor" infra-red light filter.

The light source was a 100 watt point-o-lite lamp. This lamp is used in conjunction with a resistance. Using various values of the resistance, the lamp can



V = VOLTMETER

L = POINT-O-LITE LAMP.

R = VARIABLE RHEOSTAT

FIG. 18.

operate theoretically at any voltage from 100 volts to 240 volts. In practice it is made to operate only over small voltage ranges, covering 20 volts, and the particular range of voltage used depends on the value of the resistance with the lamp connected. This means that the intensity of the illumination produced by the lamp varies from c 10% of the maximum to 100% over a range of 20 volts. It is clear that a slight change in the mains D.C. voltage can cause a large change in the intensity of the light beam incident on the film. Many of the puzzling results obtained in the earlier work were due to such changes in light intensity during the course of a series of transmission measurements.

The method finally adopted of controlling the applied voltage is due to R.A. Houston. The circuit is shown in Fig. 18. After determination of the transmission of each reflection, the voltage across the point-o-lite lamp was noted on a voltmeter connected in parallel with the lamp. Any change in the voltage was corrected by adjusting a variable rheostat set in series with both lamp and voltmeter. In this way, the voltage could be controlled to within 0.5 volt.

Step-Wedge

The current from the photocell was conducted to a Tinsley mirror galvanometer (Type 4500H). The deflection was read off a 50 cm., scale at 2 meters from the mirror. The current-deflection relationship was guaranteed linear between deflections of 5 to 45 cm. When measuring X-ray intensities from a reversed film, however, the deflections observed varied between 100 and 30,000 cm. It was clearly impossible to measure directly the intensity of even the weakest reflection. The light transmitted by the reflection had to be reduced in intensity before falling on the surface of the photocell. This was done by inserting a graduated step wedge between the film and the photocell. For any single reflection a step on the wedge was chosen such that when it was placed between the film and the photocell, the deflection lay between 5 and 45 cm.

The step wedge was graduated as follows. If I_o is the light incident on a given step and I_t the light transmitted by the step, then for the r^{th} step there will be a quantity K_r such that:

$$K_r = I_o/I_t.$$

Whence, $$I_o = K_r I_t.$$

I_o is the light transmitted by a reflection and is therefore proportional to the X-ray intensity of the reflection. A measure of I_t is given by the galvanometer deflection. Therefore in order to obtain I_o, K_r must be known.

Determination of K

The wedge used had seven steps. They were numbered 1, 2, 3 .... 7, where 1 was the least dense .. A beam of light intensity I_o was directed on to each of these steps in turn. I_1, I_2 ... I_7 were the intensities of the beams transmitted by each step.

Then, $I_o/I_1 = K_1$

and $I_o/I_7 = K_7$

Eliminating I_o from these equations,

$$K_7 = K_1 I_1/I_7.$$

Proceeding in this way, all the K's were expressed in terms of K_1.

Since the scale did not need to be absolute, i.e. since the object of the method was to measure relative X-ray intensities, K_1 could be assigned any suitable value.

The steps were graduated in this way. The same beam of light was directed onto the surface of each step in turn and I_r recorded from the galvanometer. K_r was worked out as shown above, taking $K_1 = 10$.

The values of K_r are recorded in Appendix I.

Preparation of the step wedge

The light transmitted by the reversed film passed through a hole in the plate glass base of the photometer before reaching the photocell. This hole was circular, one inch in diameter. It was necessary for each step to cover the hole completely.

A Zeiss - Ikon 35 m.m. film camera, with a 3.5 Tessar lens, gives a negative 26 x 26 m.m.^{2} in area. This is almost exactly one inch square, and so such a negative covers the hole in the glass completely. The step wedge was prepared using this camera.

The camera was loaded with Ilford Pan F 35 m.m. film. Clouds in the northern sky (northern clouds

were chosen since they are generally more evenly illuminated) were photographed through opal glass; the opal glass was necessary in order to ensure uniform exposure of the negative. Seven exposures were made with successive exposure times 1/25,1/10,1/5,1/2,1,2,4 seconds, at f/11. The exposed film was then developed carefully in Kodak "MICRODOL" fine grain developer. When dry, the film was mounted between two clean glass plates.

There was one objection which might have been made to mounting the step wedge between glass plates. Some of the light transmitted by the film was lost by reflection from the glass surface. However the quantity lost should be a constant fraction of the total light, and if this is true reflection of the light at the glass surface should not change the relative intensities recorded by the photocell. Nothing was observed to indicate that this assumption was not correct.

Measurement of Intensities

The beam from the point-o-lite lamp was adjusted until the diameter of the light spot was just sufficient to include the largest reflection on the series. Thereafter the light beam was left unaltered.

A reading of the galvanometer deflection caused by the light transmitted by the reflection and its immediate surroundings was taken first. This deflection was noted together with the step on the step wedge which had been interposed. Let this deflection be D_1. With the same step in position, the film was moved so that the light beam was incident on a blank piece of film, close to the reflection, and with the same $2\sin\theta$ value as the reflection. The galvanometer deflection caused by the light transmitted through this background was noted. This measurement was repeated on the other side of the reflection. The mean of these two deflections gave a measure of the background transmission at the reflection; in general the two readings did not differ by much. Let this mean be D_2.

Then integrated intensity of reflection $\propto K_r(D_1-D_2)$.

At the center of some of the stronger reflections on the upper films in the pack, there were areas which contained no silver. In such reflections the intensity of the reflected X-ray beam was so high

that all the silver grains in its path were activated. As a result, all the silver halide present was reduced to silver during the first development, and the silver was removed by the bleaching bath. The optical transmission in this case is no longer proportional to the X-ray intensity.

The transmission of these reflections was then measured on the lower films of the pack on which the reflections had no cleared areas. This transmission was then multiplied by the appropriate power of the film factor to give the relative integrated intensity.

The film factor found for Ilford Fast Blue Sensitive Film was 2.1.

RESULTS

In order to assess the value of the procedures previously outlined it was necessary to use them to measure the intensities of reflections which had been carefully measured by other methods, and to compare the two sets of values.

At the suggestion of Professor J.M. Robertson, the reflections from the h0l planes of anthracene crystals were examined. The intensities of these reflections had been carefully measured, and the structure factors recorded in the literature[14]. Packs of film, containing five films each, were exposed to the h0l reflections from two different crystals of anthracene. These packs were labelled R.S. 18 and R.S. 19.

In the measurement of these intensities, the previous workers had applied corrections to the intensity data for the absorption of X-rays by the crystal. The corrections were not recorded, and so it was not possible to convert the recorded structure factors back into intensities. Accordingly, the intensities measured by the reversal process were converted to structure factors, and the various

sets of structure factors were compared, rather than intensities.

Anthracene - R.S. 18

Five Ilford Fast Blue Sensitive X-ray films were exposed in a pack for 52 hours to the hOl reflections from a crystal of anthracene with dimensions 1.3 x 0.5 x 0.2 m.m. CuK radiation was used; it was generated by a North American Philips sealed tube operating at a filament current of 15 m.amp., and a voltage of 30 kv. A six step wedge was superimposed. The films were processed by the procedure outlined on p. 41 . The second development time was 4 minutes and 20 seconds at 18.0°C. The characteristic curves measured on these films are shown in Fig. 16.

Anthracene - R.S. 19

Five Ilford Fast Blue-Sensitive X-ray films were exposed in a pack for 49 hours to the hOl reflections from an anthracene crystal with dimensions 1.5 x 0.7 x 0.3 m.m. CuK radiation was used; it was produced by a North American Phillips sealed tube operating at a filament current of 15 m. amp., and a voltage of 30 kv. A six step wedge was superimposed. The films were processed by the procedure outlined on

p. 41 , with a second development time of 4 minutes at 18.0° C. The characteristic curves measured on these films are shown in Fig. 14.

The two anthracene crystals used were members of the same batch grown by evaporation at room temperature of a concentrated solution of anthracene in amyl acetate. The anthracene crystallised in well formed prisms elongated along the b axis.

The structure factors derived from the reversal of these multiple film packs are recorded in Table 1. The values for the reflections 200 and $20\bar{1}$ are not recorded because on each of the five films in each pack the images of these reflections contained clear spots. The reflection 001 was not measured since the beam trap in the camera partially cut off the reflection.

Table 1

Observed Structure Factors for (h0l) Zone in Anthracene

Plane	F_o R.S.18	F_o R.S.19	F_o Robertson et al.[14]
*002	20.8	21.2	23.7
003	14.4	13.9	14.0
*004	20.8	21.5	24.6
*005	16.2	16.2	16.9
006	6.0	7.0	6.0
*20$\bar{2}$	24.9	25.6	25.5
20$\bar{3}$	13.7	14.7	14.5
20$\bar{4}$	3.2	3.3	3.3
20$\bar{5}$	5.0	5.0	5.0
20$\bar{6}$	5.2	5.2	5.4
20$\bar{7}$	4.3	4.2	4.4
20$\bar{8}$	3.1	3.1	2.6
20$\bar{9}$	11.4	10.8	9.2
201	5.4	5.5	4.5
202	4.1	4.2	4.3
203	4.8	4.6	4.4
*204	24.2	24.3	25.5
205	9.4	9.2	9.3
400	3.8	4.3	3.9
40$\bar{1}$	3.4	3.5	3.5

Table 1 (contd.)

Plane	F_o R.S.18	F_o R.S.19	F_o Robertson et al.
$40\bar{2}$	6.7	6.8	6.3
$40\bar{3}$	7.0	6.6	6.2
$40\bar{5}$	12.0	11.5	12.3
$40\bar{6}$	5.1	5.1	5.0
$40\bar{7}$	5.3	5.0	5.2
*$40\bar{9}$	24.2	23.3	26.6
$40,\bar{10}$	10.5	11.0	10.3
402	4.1	3.8	3.7
403	7.8	8.0	7.6
404	7.8	7.4	8.4
600	9.6	8.8	7.3
*$60\bar{1}$	15.1	15.2	11.2
$60\bar{3}$	3.6	4.7	4.9
$60\bar{4}$	3.8	4.1	4.6
*$60\bar{5}$	20.2	19.8	20.6
$60\bar{6}$	5.9	5.9	5.3
*$60\bar{9}$	18.2	17.4	16.4
*$60,\bar{10}$	17.9	17.3	16.6

The discrepancy between the structure factors measured from R.S.18 and the structure factors measured by Robertson et al., calculated by the expression $\frac{\sum||F_o'| - |F_o||}{\sum|F_o|} \times 100$, is 8.6%

The discrepancy between the structure factors measured from R.S.19 and those measured by Robertson et al., is 7.7%.

The discrepancy between the structure factors measured from R.S.18 and those measured from R.S.19 is 3.6%.

F_o' is structure factor obtained from a reversed pack of film.

F_o is structure factor obtained by Robertson et al.

FINAL DISCUSSION

The first object of this research was to obtain positives of X-ray crystal diffraction photographs by photographic reversal. It was necessary that the characteristic curves of these films should be linear from the origin over a large part of their range. The second object was to produce a reversal technique in which there were fewer critical steps than in the Dawton printing process. Both objectives were attained in the final procedure outlined on page 41.

The reversal technique for measuring intensities possesses the usual advantages of photographic methods; the films give a permanent record of the reflections, indexing the reflections is easy, and checking the value of the intensity of any reflection is not difficult.

The outstanding feature though of this method is the high rate at which intensities can be measured. The time necessary to measure the intensity of a reflection is simply the time required to take two photometer readings and to record them in a note book. In the case of copper tropolone (which will be discussed in Part II) 120 reflections were

measured up and checked in three hours. The visual measurement and checking of these same reflections on direct films took about thirty-five hours.

Against this speed in the measurement of the intensities must be set two factors. So far it has been possible to work out a reversal procedure only for Ilford Fast Blue-Sensitive X-ray Film. This is a single coated film and has a film speed about one half that of the double coated Ilford Industrial G X-ray Film[15]. The latter is the film normally used in Britain when the intensities are to be estimated visually. Also, when any film is to be reversed it must be given twice the exposure required to produce a good negative[15]. Therefore if a certain number of reflections are observed on an Ilford Industrial G X-ray Film negative, Ilford Fast Blue-Sensitive Film must be given four times the exposure in order to have the same number of reflections observed on the reversed films. Thus, where long exposures are required, the time which will elapse between first putting the film in the camera and obtaining the intensities will be much the same whether we use the reversal method with Fast Blue-Sensitive X-ray Film

or the visual estimation method with Industrial G X-ray film.

However there is one point that must be borne in mind. Whenever it is necessary to give the Fast Blue-Sensitive X-ray Film a long exposure useful work can be done meanwhile. Apart from occasional trips into the laboratory to inspect the camera and tube, the operator is free to carry on with other work. The additional exposure time need not be time wasted. However during the long and tedious visual estimation of intensities from negatives other useful work cannot be done. Although in some cases it might take just as long to obtain the intensities of a zone of reflections by the reversal technique as by visual estimation, the man using the reversal technique can use the time more efficiently.

Accuracy of the Results

Structure factors derived from visually estimated intensities can generally be relied upon to be accurate to within 5 - 10%. In the case of the structure factors measured for anthracene there is a discrepancy

of 7.7% between the measurements of Robertson et al.,[14] and the measurements made from the R.S.19 reversed pack. Although the former of the two sets of measurements is very accurate they will be in error to some small extent. Suppose that the discrepancy between these measurements and the true values of the structure factors is d%. Then by adding the discrepancies, we find that the maximum error associated with the measurements made on the reversed films is (7.7 + d) %; the minimum error is given by the difference of the discrepancies, and is (7.7 - d) %. The value of d cannot be determined since its evaluation would require exact intensity data and a full knowledge of the extinction of the radiation caused by the crystal during reflection of the X-ray beam. However an estimate can be made, and in this case a value of 3 for d would not be unreasonable. With this value of d the discrepancy between the values of the structure factors of the anthracene reflections measured from the reversed films of R.S.19 and their true values would lie between 4.7 and 10.7 %. This places the discrepancy between the limits of accuracy of the visual estimates. The same may be said of the structure factors measured from the reversed films of R.S.18.

Reproducibility of the Measurements

The discrepancy between the structure factors measured from the reversed films of R.S.18 and those measured from the reversed films of R.S.19 is 3.6 %. This agreement is good considering that the comparison is being made between two different exposures processed at different times. Two different visual estimates of intensity, from the same films, are considered to be adequate if they agree to within 10%, i.e. if the structure factors agree to within 5%. Measurements of intensity made at different times on the same reversed films agree to within 1 - 2%; this of course is the photometer error.

Accuracy of Measurement in the Stronger Planes

If we select from the list on pages 31-32 the planes with structure factors greater than 15.0 (indicated by a *) and compare the values of the structure factors measured from reversed films of R.S.18 and R.S.19 we see that the discrepancy between them is 2.0%. Since the discrepancy over all planes is 3.6% it would seem that the reversal technique is

slightly more accurate for the stronger reflections. This is probably due to the fact that in the case of a strong reflection the transmission through the reflection is much larger than the background transmission. Thus the relative intensity of the plane is the difference between a large and a small quantity, and so can be more accurately measured than the difference between two nearly equal quantities. In the case of the weaker reflections we must measure the difference between two small and nearly equal quantities.

There is one disappointment that must be recorded. It had been hoped that the reversed film would possess a characteristic curve linear from the origin to a high transmission. Unfortunately the characteristic curve begins to deviate from a straight line at transmissions greater than 65-70%. However when a multiple film technique is being used this is not too serious. Suppose that on the most heavily exposed film of a reversed multiple film pack a reflection has a relative intensity of I_a, and that on the next film of the pack the same reflection has a relative intensity of I_b. Then

I_a/I_b should be equal to the film factor, 2.1. If the ratio is less than 2.1 then the reflection on the more highly exposed film, or on both films, contains points of optical transmission greater than 65%. Successive films can be compared in this way until the ratio of the relative intensities is close to 2.1. In this way for every reflection a film is found on which no point in the reflection has a transmission greater than 65-70%. The intensity for the reflection measured from the selected film is then multiplied by the appropriate power of the film factor.

Photometer

The photometer used was ideally suited for the purpose. However, as has already been noted (p 44), the intensity of the light beam fluctuated widely with change in D.C. voltage. The stabiliser used (p. 44) was adequate, but cumbersome. It could be replaced with advantage by an automatic electronic voltage regulator.

The lenses used in the construction of the photometer were not of the highest quality. If they were to be replaced by achromatic lenses then the intensity measured across the incident light beam would be more uniform. This would reduce the photometer error slightly.

APPENDIX I

Step constants for the step wedge used in conjunction with the photometer used for measuring the intensities of X-ray crystal reflections from reversed films (Pages 45-46).

Step	Constant
1	10.0
2	14.4
3	24.4
4	46.5
5	63.5
6	92.5
7	120.1

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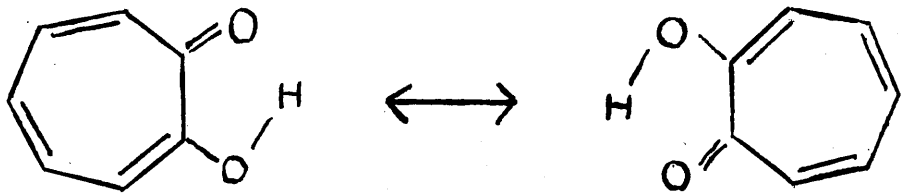
PART II

Crystallographic Studies on some Tropolones.

THE CRYSTAL AND MOLECULAR STRUCTURE OF COPPER TROPOLONE

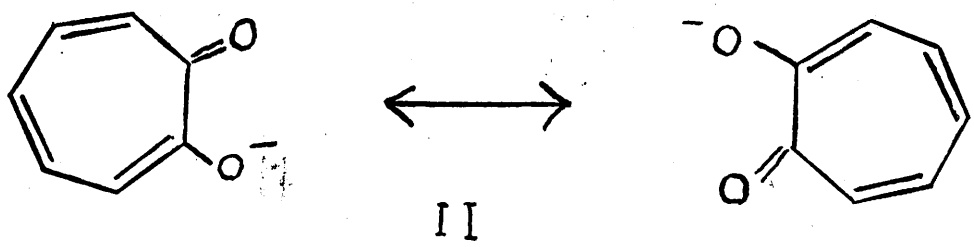
Tropolone was first discussed in 1942 by Raistrick and his coworkers[1]. It was shown to be a seven-membered carbon ring with a ketonic oxygen atom and a hydroxyl group substituted on adjacent carbon atoms. This compound was found to have considerable aromatic character. Like benzene it has a number of structural formulae of comparable energy which could contribute to a resonance formulation of its structure. For example, if the following unexcited structures were considered to be



I

the dominant contributors to the resonance hybrid, then the ring would contain six C - C bonds of equal length; the bond between the carbon atoms carrying the oxygen atoms does not enter into the resonance as postulated above, and would be expected to be more nearly a normal C - C single bond. This picture is more likely to be true in the case of the tropolone anion in which the

difficulty of having the hydrogen atom bonded to two different oxygen atoms does not arise:



II

The first structural study of any tropolone was carried out by J.M. Robertson[2,3] in 1950 with his analysis of cupric tropolone. This was a study of the tropolone anion under the influence of the positive cupric ion. A second study of the tropolone anion was published in 1956 by Nitta and his co-workers; they studied sodium tropolone[4]. In both cases the average C - C distance around the ring was found to be 1.41 A. In the sodium salt the C - O distances were found to be equal, but in the copper salt a difference in the C - O distances was found (0.15 Å) which was greater than the sum of the estimated deviations in the distances (0.06 Å).

Various other tropolones have also been investigated, bromotropolone[5], nootkatin[5], tropolone hydrochloride[6], tropone[7]. The results of these investigations are

consistent with the model of a regular planar ring with a C - C distance of 1.41 Å.

However, only in the case of sodium tropolone and tropolone hydrochloride was the analysis of high accuracy. For example in copper tropolone the estimated standard deviation of the bonds was 0.03 Å. The analysis was confined to the (hko) zone of reflexions in which only 57% of the total number of possible reflexions was observed. No series-termination correction was applied, and the thermal parameters were not refined. By 1954 sodium tropolone was commercially obtainable and it was possible to prepare large quantities of copper tropolone. As a result larger crystals of copper tropolone became available, and it was decided to repeat the analysis of copper tropolone.

It was felt that the time was opportune for two reasons. With larger crystals it would be possible to record a larger proportion of the reflexions within the reflecting sphere. The second reason was that new and accurate theoretical scattering curves were now available. Using these instead of empirical curves it would be possible to refine the thermal parameters

exactly. These factors would combine to yield more accurate atomic coordinates.

Growth of Crystals

Copper tropolone was prepared by mixing 10% solutions of sodium tropolone and copper sulphate. The volumes of the solutions were fixed so that each contained an amount of reagent equivalent to that contained by the other. The precipitate of copper tropolone was filtered off and washed with water. This micro-crystalline material was dried between filter papers and dissolved in ethanol. The crystals were grown by slow evaporation of ethanol at room temperature. Under these conditions the crystals tended to grow in clusters, but a number of fine single crystals were isolated.

The crystals grew as long needles elongated along the C-axis. In some batches a few more lath-shaped crystals were observed, and these were used in the intensity measurements since they were slightly larger.

Crystal data

$(C_7H_5O_2)_2Cu$ Molecular weight : 305.8

d_{obs} : 1.696 d calc : 1.683

Monoclinic: a = 11.60±0.05 Å b = 13.82±0.02Å c=3.80±0.005Å

$\beta = 93.4°$

Absent spectra: (h0l) when h is odd.

(0k0) when k is odd.

Space group : C_{2h}^5 - P21/a

Two molecules per unit cell.

Molecular symmetry : centre.

Volume of the unit cell : 608Å^3.

Total number of electrons per unit cell: 310.

These data were determined by Robertson[2] and checked during the present investigation.

Experimental Measurements

The reflections of the (hko) zone were recorded first on two multiple film packs using a Weissenberg moving film camera. Each pack contained five Ilford Industrial G x-ray films. The first pack was given an exposure of 15 hours, and the second an exposure of 51 hours; both packs were exposed to the radiation from a sealed tube operating at 30 kv., and 10 m. amp., filament current. These packs were developed directly. The crystal with which these exposures were made measured 1.5 x 0.2 x 0.1 $m.m^3$. It was necessary to expose two packs since someof the stronger planes were overexposed, even on the bottom film of the pack,and so their relative intensities could not be measured on the pack given the longer exposure. On both packs the intensities of all measureable reflections were estimated visually. The intensities were placed on the same relative scale by comparison of reflections common to both packs. These intensities were then converted to structure factors using the mosaic crystal formula[8].

The (hko) zone reflections were also recorded on a third pack of five films on a Weissenberg camera. The films were Ilford Fast Blue-Sensitive X-ray films.

This pack was given an exposure of 100 hours on a sealed tube operating under the same conditions as before. These films were reversed using the photographic reversal process described in the first part of this thesis. A second development time of 4 min. 15 sec. at 18°C was given. The crystal used had dimensions 1.25 x 0.14 x 0.09 m.m.^{3}. The relative intensities of the reflections were measured from the films using the photometer described earlier, with the DC voltage maintained at 228 volts. These intensities were converted to structure factors using the mosaic crystal formula.

In all three multiple film packs the films were separated from one another by two thicknesses of black paper. All exposures were made using CuK unfiltered radiation; unfiltered radiation was used in order to reduce exposure times.

Comparison of Observed Structure Factors

In Table 1 appear the structure factors derived from the reversed films, together with the corresponding structure factors derived from the two packs processed

TABLE 1

Comparison of structure factors derived from three independent measurements.

Fmp - structure factors derived from reversed films.

Fmv - structure factors derived from films given direct development.

Frv - structure factors reported by Robertson.

Plane	Fmp	Fmv	Frv	Plane	Fmp	Fmv	Frv
110	-	91	74	250	40	40	37
120	60	65	57	260	48	46	37
130	58	61	46	270	11	12	16
150	40	37	33	280	36	35	30
160	9	8	-	2,10,0	34	31	37
170	68	71	55	2,11,0	11	11	13
190	36	31	30	2,12,0	13	12	17
1,10,0	8	10	-	2,13,0	11	10	16
1,11,0	9	8	-	2,14,0	11	10	15
1,12,0	10	11	11	2,16,0	5	7	12
1,13,0	12	14	16	310	36	40	24
200	5	6	9	320	34	37	35
210	7	7	13	330	37	37	37
220	49	51	39	340	27	27	21
230	12	14	3	350	24	24	22
240	4	6	4	360	41	40	35

TABLE 1 (contd.)

Plane	Fmp	Fmv	Frv	Plane	Fmp	Fmv	Frv
370	41	27	30	620	37	37	41
380	15	16	14	630	10	10	11
390	23	21	23	640	42	46	49
3,11,0	26	24	26	660	26	23	25
400	10	11	-	680	18	20	25
410	6	9	5	710	26	26	32
420	28	28	25	730	35	42	37
440	42	45	34	750	28	27	32
460	19	19	19	770	29	31	26
480	21	22	17	820	26	23	27
490	13	13	15	840	20	19	26
4,10,0	15	16	16	850	13	15	21
510	39	40	40	860	23	22	26
520	20	21	18	930	27	28	37
530	6	9	9	950	19	21	32
550	36	30	28	020	61	66	53
590	28	21	26	040	74	65	65
600	45	50	43	060	32	37	26
610	20	18	25	080	53	55	54

70 planes are listed in Table 1. F(110) could not be obtained from the reversed pack since its image was over-exposed on all five films.

TABLE 1 (contd.)

Let $D(a,b) = 100 \Sigma \left| |F_a| - |F_b| \right| / \Sigma |F|$

Then, D(mp,mv) = 7.7%

D(mv,rv) = 18.2%

and D(mp,rv) = 16.9%

D(a,b) is referred to as the discrepancy between the two sets of measurements.

directly and those reported by Robertson[2]. The three sets of figures were placed on the same scale by comparison of the first two with the third. It will be seen that the structure factors derived during the present investigation, while they agree quite well within themselves (7.7%), show poor agreement with those derived earlier (17%-18%).

It is very difficult to account for this poor agreement. The intensities of the reflections recorded on the films which were processed directly were estimated visually three times by the writer, and once by Mr. R. Bryan of this department. The structure factors so derived agreed within themselves to about 6-7%, but in each case they showed a discrepancy of 15-20% with the structure factors reported by Robertson.

A survey of the reflections shows that the largest discrepancies tend to be concentrated in the strong planes of low sin θ values, e.g. 110,020, while agreement is better in planes like 750,080, with comparatively high sin θ values. This would suggest that perhaps the film factor was a bit wrong in one or other of the determinations of intensity.

In the visual estimation of the intensities by the writer the film factor was not measured. A value of 3.3

was used. This value had been used by other workers in this department for some time with good results. In the photometric measurement of the intensities the film factor was measured. The measure of agreement between these two sets of figures suggests that the value of 3.3 used in the first case for Ilford Industrial G film is not too far wrong, if at all.

In the earlier visual estimation of the intensities[2], the film factor was measured. Thus the film factor seems to be disposed of as a possible source of error.

If one or other of the samples from which the crystals were prepared happened to be rather impure, then this would lead to differences in the observed structure factors. It is impossible at this time to check this possibility directly. Errors due to large amounts of impurity in the crystal would modify the representation of the molecule given by a Fourier synthesis. However Fourier maps derived both from the current data (see later) and Robertson's data[2] show perfectly resolved atoms, and only one or two small electron density maxima which cannot easily be interpreted as atoms. In particular there is no sign of solvation of the crystals.

Structure Refinement

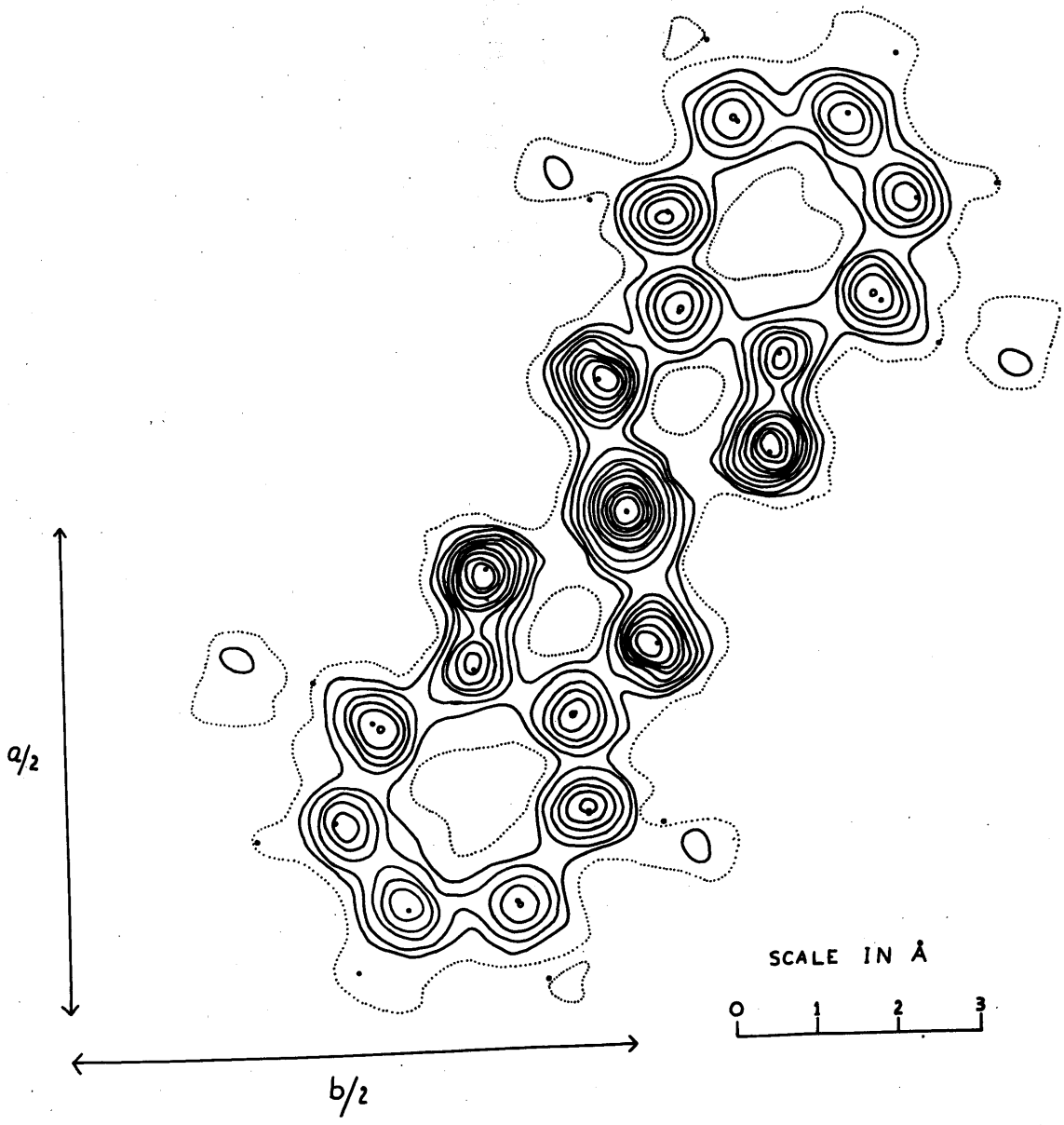
a) Fourier Synthesis

As a first step in the refinement of the structure of copper tropolone a Fourier synthesis was made. The coefficients used were the structure factors derived by visual estimation of the intensities of the reflections recorded on the direct films. These measurements were used rather than those derived from the reversed films because they were more numerous. A total of 154 reflections was observed out of a possible 208 within the reflecting circle of CuK radiation, a yield of 75%. This should be compared with a yield of 57% in the earlier work[2].

The phases of the structure factors for which $\underline{h} + \underline{k}$ is odd are not determined by the copper atom at the centre of symmetry. The phases of these planes were calculated using the atomic coordinates and atomic scattering curves listed by Robertson[9].

By the end of the refinement there were no further changes in phase, and so the electron density map given by this synthesis is the final map. It is shown in Fig. 1.

It will be observed from the map that the hydrogen



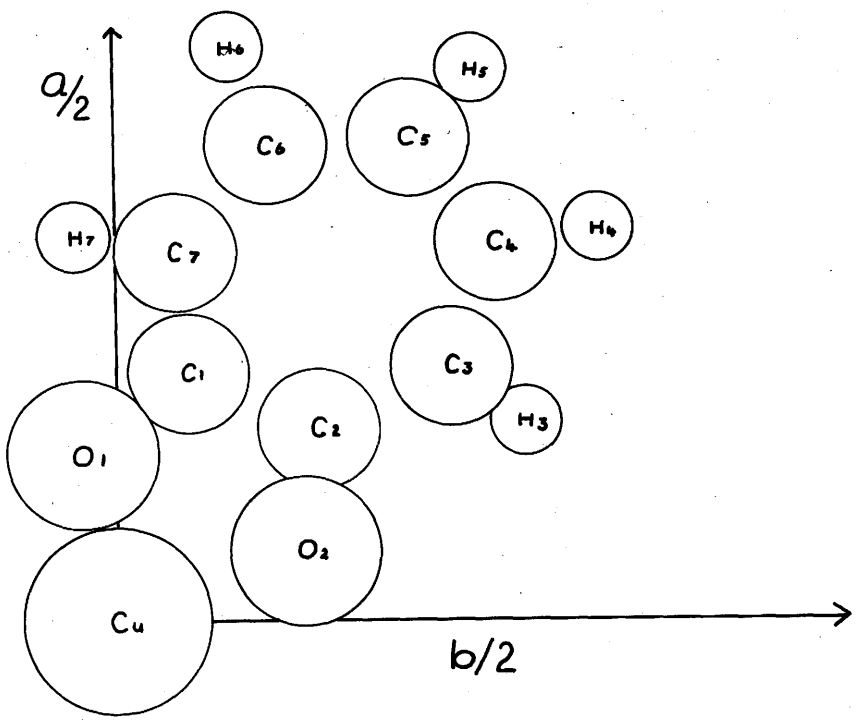
CUPRIC TROPOLONE FIG. 1.

LARGE DOTS SHOW FINAL ATOMIC CENTRES

CUPRIC TROPOLONE

FIG. 2.

ATOM NUMBERING SYSTEM



atoms show up very well. However beside each of the α-carbon atoms there is a small two-electron peak. Although they are in the general area in which the hydrogen atoms might be expected to exist, they are too far away from the carbon atoms to correspond exactly to hydrogen atoms. It is rather difficult to explain the occurrence of these peaks. The explanation probably lies in a combination of factors such as diffraction effects due to the heavy copper atom and errors introduced by terminating the Fourier series. Also, there is no doubt that the presence of the hydrogen atoms in the same general area will cause a noticeable increase in the electron density near the two-electron peaks.

The atomic positions shown on the map are those obtained from the final least-squares refinement from the initial positions.

Refinement of Structure

The structure was refined by least squares procedures using an IBM 704 electronic computer. The computer is described briefly in Appendix II. The refinement was carried out in two parts. In both parts atomic

coordinates were varied together with temperature parameters. However, to begin with the thermal motion of the atoms was assumed to be isotropic, and only one temperature parameter was refined for each atom. After these individual isotropic thermal parameters had converged, initial values of the more general anisotropic thermal parameters were deduced from them. The best anisotropic thermal parameters and atomic coordinates were then fitted to the data during the second part of the least squares procedure.

Least Squares Approximation

The method of least squares was first used in the refinement of a crystal structure by Hughes[10]. The mathematics of the technique have been discussed by Whittaker and Robinson[11], and Lipson and Cochran[12] have published an excellent review of it from the viewpoint of the crystallographer.

Least squares approximation is one of the applications of Taylor's Theorem. Suppose we have a function of n variables, $F(x_1, x_2, \text{----}, x_n)$. Suppose further that the value of the function is Fc when the variables have the values $x_1, x_2, \text{----}, x_n$ and the value Fo when

the variables have the values $(x_1 + \Delta x_1)$, $(x_2 + \Delta x_2)$. ---- $(n_n + \Delta x_n)$, where Δx_1, Δx_2, ----, Δx_n are small. Then Taylor's theorem states that, to a first approximation,

$$Fo = Fc + \left(\Delta x_1 \frac{\partial Fc}{\partial x_1} + \Delta x_2 \frac{\partial Fc}{\partial x_2} + \ldots + \Delta xn \frac{\partial Fc}{\partial xn} \right) + \ldots \quad (1)$$

Thus we have a relation between true and slightly false values of the function in terms of the corrections which must be applied to the variables to bring the value of the function to its true value.

Now suppose we can assign q different sets of coefficients to the variables x_1, x_2, ----, x_n in the function. For a given set of variables we will obtain q values of the function. If $q = n$, then the q equations similar to (1) can be solved to give the corrections Δx_1, Δx_2, ----, Δx_n which must be applied to the variables to make Fc = Fo. If $q < n$ then we have fewer than n simultaneous equations and thus an infinite number of solutions to these equations.

In the case where $q > n$ it should be possible to find only n independent equations which could then be solved in the usual way. However when this reasoning

is applied to practical observations a difficulty arises. Experimental observations are always inaccurate, even if only slightly so. Therefore, if Fo in equation (1) corresponds to an experimental observation, then the q equations resulting will be inconsistent. This inconsistency is overcome in the method of least squares in the following way. Each of the q equations is taken in turn and is multiplied throughout by the coefficient of Δx_1 in that equation. The resulting q equations are then added together to give one equation of the type:

$$\sum^{q}\frac{\partial Fc}{\partial x_1}\,Fo = \sum^{q}\frac{\partial Fc}{\partial x_1}\,Fc + \Delta x_1\sum^{q}\left(\frac{\partial Fc}{\partial x_1}\right)^2 + \text{----} + \Delta x_n\sum^{q}\left(\frac{\partial Fc}{\partial x_1}\right)\left(\frac{\partial Fc}{\partial x_n}\right). \quad (2)$$

This process is repeated with the original equations but using the appropriate coefficients of Δx_2, Δx_3, and so on, until n equations of the type of equation 2 are obtained. These n equations are independent and form a consistent set and can be solved exactly to give Δx_1, Δx_2, ----, Δx_m. Equations of the type I have been called "observational equations" by Whittaker and Robinson. Those of type 2 they termed "normal equations."

Application of the least squares approximation to X-ray analysis

In equations (1) and (2) consider Fo as representing the observed structure factor, and Fc as representing the calculated structure factor. Then Δx_1, Δx_2, ----, Δx_n represent the corrections which must be applied to the atomic coordinates and the thermal parameters in order to bring Fc as closely as possible to Fo. An X-ray analysis is not undertaken unless the number of independent planes observed is much larger than the number of variables involved. It is in a situation such as this that the method of least squares is applied, and the greater the number of independent planes observed the better will be the results obtained from the procedure.

For use in a structural problem the conditional equations should be written in the form:

$$\Delta x_1 \frac{\partial Fc}{\partial x_1} + \Delta x_2 \frac{\partial Fc}{\partial x_2} + \cdots\cdots + \Delta x_n \frac{\partial Fc}{\partial x_n} = (Fo - Fc)$$

The normal equations will then be of the form:

$$\Delta x_1 \sum^{q} \left(\frac{\partial Fc}{\partial x_1}\right)^2 + \cdots\cdots + \Delta x_n \sum^{q} \left(\frac{\partial Fc}{\partial x_1}\right)\left(\frac{\partial Fc}{\partial x_n}\right) = \sum^{q} \left(\frac{\partial Fc}{\partial x_1}\right) (Fo - Fc)$$

and we obtain a set of equations linear in the corrections to the parameters. Herein lies the one mathematical limitation to the method of least squares. In the expansion of the Taylor's Series to obtain equation (1), all powers of the Δx's higher than the first were ignored. This approximation is justifiable only when the Δx's are small. Therefore the method of least squares should be used only when fairly accurate parameters have already been obtained in some other way. The method of least squares, as it stands, cannot be used to solve an unknown structure.

Weighting

The measurements of Fo are not accurate. However, it is often possible to say that the intensity of some planes has been measured more accurately than the intensities of other planes. If an estimate of the difference in the accuracy of the measurements can be made, then this can be included in the least squares procedure as a weighting factor applied to the conditional equations. In general the weighting factor will be different in each observational equation. Then the normal equations will be of the form:

$$\Delta x_1 \sum^{q} Wq\left(\frac{\partial Fc}{\partial x_1}\right)^2 + \ldots\ldots + \Delta x_n \sum^{q} Wq\left(\frac{\partial Fc}{\partial x_1}\right)\left(\frac{\partial Fc}{\partial x_n}\right) = \sum^{q} Wq\left(\frac{\partial Fc}{\partial x_1}\right) \quad (Fo-Fc)$$

where Wq is the weight to be given to the qth observation. Wq will have a value from zero to one.

Further approximations

So far in this discussion it has been assumed that the final step in a least squares refinement is the solution of a set of n simultaneous linear equations. In principle this is true, but in practice it is very difficult. If we take even a simple case of a structure with ten atoms in the unit cell ninety parameters are required to describe it fully. This would lead in a least squares approximation to a set of ninety differential equations. The arithmetical difficulties involved in the solution of such a set would be severe, even with the help of an electronic computer. Also owing to the termination of the Taylor's Series, the solution of the equations will not yield the true parameters; it is always necessary to reiterate the least squares procedure until further iteration yields no further

change in the parameters.

Various approximations have been employed to reduce the amount of arithmetical work required to obtain the corrections from the normal equations. The most drastic of these assumes that those coefficients in the normal equations of the type $\sum^{q} Wq\left(\frac{\partial Fc}{\partial x_1}\right)\left(\frac{\partial Fc}{\partial x_2}\right)$ - the cross terms - are always much smaller than those of the type $\sum^{q} Wq \left(\frac{\partial Fc}{\partial x_1}\right)^2$ - the diagonal terms - and can be neglected in comparison. This approximation yields normal equations of the type:

$$\Delta x_1 \sum^{q} Wq\left(\frac{\partial Fc}{\partial x_1}\right)^2 = \sum^{q} Wq\left(\frac{\partial Fc}{\partial x_1}\right)(Fo - Fc)$$

$$\vdots \qquad\qquad \vdots$$

$$\Delta x_n \sum^{q} Wq\left(\frac{\partial Fc}{\partial x_n}\right)^2 = \sum^{q} Wq\left(\frac{\partial Fc}{\partial x_n}\right)(Fo - Fc)$$

These equations can be solved immediately.

This approximation, known as the diagonal approximation, is valid only when the axes are orthogonal, or nearly so. When the axes are non-orthogonal then intra-atom cross terms ought to be included in the normal equations. In a projection in which the atoms are not well resolved then the inter-atom cross terms ought to be included as well.[13]

Application of Least Squares refinement to copper tropolone

The problem being considered here is the refinement of the parameters of copper tropolone in the (hko) zone. The first question to be answered was which approximations could be made in the normal equations. The Fourier map of the (hko) projection (Fig. 1) showed that all the atoms were well resolved from one another. Therefore it was assumed that the inter-atom cross terms would be comparatively small. Also the axes were almost orthogonal, and so the intra-atom cross terms were neglected. It was therefore decided to use only the diagonal terms in the least squares matrix even although a high speed electronic computer was being used to carry out the calculation.

When the normal equations are solved without any approximations being made, two or three iterations are necessary before the best fit of the parameters to the data is found. When the diagonal approximation is made it is not uncommon for fifteen or twenty iterations to be required to reach the same result. However the latter process requires less time. Therefore, in cases where the diagonal approximation is valid the final result is

achieved more quickly by making use of it[14]. Some workers believe that it is quicker to use the diagonal approximation even when the axes are not orthogonal[14].

All observations were given the same weight.

Derivation of differentials

a) Differentials of atomic coordinates

In the space group $P2_1/a$ the structure factor for the plane hkl is defined by the expression:

$$Fc(hkl) = 4\sum_{1}^{n} f_i(hkl)\cos 2\pi\left(hx_i+lz_i+\frac{h+k}{4}\right)\cos 2\pi\left(ky_i-\frac{h+k}{4}\right)$$

where n = the total number of atoms in the asymmetric unit,

$f_i(hkl)$ = atomic scattering factor of the atom i for the plane hkl, corrected for the thermal vibration of the atom

and X_i, y_i, Z_i = coordinates of the atom i expressed in terms of fractions of the unit cell edges.

In the (hk0) zone this expression reduces to:

$$F_c(hk0) = 4\sum_{1}^{n} f_i(hk0)\cos 2\pi\left(hx_i+\frac{h+k}{4}\right)\cos 2\pi\left(ky_i-\frac{h+k}{4}\right) \quad \ldots\ldots (3)$$

Then:

$$\frac{\partial Fc(hk0)}{\partial x_i} = -8\pi h f_i(hk0)\sin 2\pi\left(hx_i+\frac{h+k}{4}\right)\cos 2\pi\left(ky_i-\frac{h+k}{4}\right)$$

$$\frac{\partial Fc(hk0)}{\partial y_i} = -8\pi k f_i(hk0)\cos 2\pi\left(hx_i+\frac{h+k}{4}\right)\sin 2\pi\left(ky_i-\frac{h+k}{4}\right)$$

Thus for each atom in the asymmetric unit, with the exception of the copper atom, two differentials of the above type were calculated for each observed plane. The differentials of the copper atom were not required since its position was known exactly.

b) Differentials of isotropic temperature parameters

Equation 3 can be rewritten:

$$Fc(hk0)=4\sum_{i}^{n} f_{o_i}(hk0)\exp(-B_i \sin^2\theta/\lambda^2)\cos 2\pi(hx+lz+\frac{h+k}{4})\cos 2\pi(ky-\frac{h+k}{4})$$

where fo_i = scattering factor for the $i^{\underline{th}}$ atom in the plane hkl when the atom is at rest,

B_i = Debye - Waller isotropic temperature factor for the $i^{\underline{th}}$ atom,

θ = Bragg angle

λ = wavelength of the radiation used,

and the other variables have the same meaning as before.

Then,

$$\frac{\partial Fc(hk0)}{\partial B_i} = -4\sin^2\theta/\lambda^2 fo_i(hk0)\exp(-B_i \sin^2\theta/\lambda^2)\cos 2\pi(hx+lz+\frac{h+k}{4})\cos 2\pi(ky-\frac{h+k}{4})$$

For each of the ten atoms in the asymmetric unit, including copper, differentials of the above type were calculated for each plane.

c) Differentials of anisotropic temperature parameters

(i) Derivation of initial anisotropic parameters

The form of the correction for anisotropic thermal motion which is most suitable for refinement by least squares methods is that given by Rollett and Davies[15], viz.,

$$\exp - (h^2\alpha + k^2\beta + l^2\gamma + hk\delta + kl\epsilon + hl\eta) .$$

The correction for isotropic thermal vibration was expressed in the form $\exp -B\sin^2\theta/\lambda^2$. Now, the isotropic correction represents an averaged out anisotropic correction and it is legitimate to say that, as a first approximation,

$$(B\sin^2\theta)/\lambda^2 \equiv B(h^2a^{*2}+k^2b^{*2}+l^2c^{*2}+2hka^*b^*\cos\gamma^*+2klb^*c^*\cos\alpha^* + 2hlc^*a^*\cos\beta^*)/4$$

$$\equiv h^2\alpha+k^2\beta+l^2\gamma+hk\delta+kl\epsilon+hl\eta.$$

From this identity we can obtain the initial values of the anisotropic thermal parameters which are:

$$\alpha = Ba^{*2}/4$$

$$\beta = Bb^{*2}/4$$

$$\gamma = Bc^{*2}/4$$

$$\delta = Ba^*b^*\cos\gamma^*/2 = 0 \qquad (\cos\gamma^* = 0)$$

$$\epsilon = Bb^*c^*\cos\alpha^*/2 = 0 \qquad (\cos\alpha^* = 0)$$

$$\eta = Bc^*a^*\cos\beta^*/2$$

Thus in a monoclinic space-group the correction for anisotropic thermal motion has the form, $\exp -(h^2\alpha+k^2\beta+l^2\gamma+hl\eta)$. In the (hk0) projection this takes the form $\exp -(h^2\alpha+k^2\beta)$ since $l = 0$ over all the planes.

(ii) Differentials

The structure factor for the (hk0) zone in the space group $P2_1/a$ can now be expressed as follows:

$$F_c(hk0) = 4\sum_{1}^{n} fo_i \exp -(h^2\alpha_i+k^2\beta_i)\cos 2\pi(hx_i+\frac{h+k}{4})\cos 2\pi(ky_i-\frac{h+k}{4})$$

Then if $\phi = 4fo_i \exp -(h^2\alpha_i+k^2\beta_i)\cos 2\pi(hx_i+\frac{h+k}{4})\cos 2\pi(ky_i-\frac{h+k}{4})$,

$$\frac{\partial Fc(hk0)}{\partial \alpha_i} = -h^2\phi_i ,$$

and

$$\frac{Fc(hk0)}{\partial \beta_i} = -k^2\phi_i .$$

Refinement of atomic coordinates and isotropic thermal parameters

The atomic coordinates were refined first using a program (NYXRI) designed for the refinement of isotropic thermal parameters and atomic coordinates by least squares procedures[16]. The computations with this program were very kindly carried out by Dr. Sayre of the IBM Corporation, New York.

The initial atomic coordinates used in the analysis were derived from the Fourier map shown in Fig. 1. The initial values of the B factors were arrived at by guesswork. Ferrocene seemed to have a melting point and other physical properties similar to copper tropolone, and the iron atom was in a similar crystallographic position. The isotropic temperature factor of the iron atom had been reported as 3.0 at room temperature[17]. Accordingly, as a starting point, the copper atom was assigned a B-factor of 3.0 $Å^2$. Since the carbon and oxygen atoms were lighter than the copper atom, it was assumed that the amplitude of their thermal vibrations was greater than that of the copper vibrations. The carbon and oxygen atoms were then arbitrarily assigned initial B-factors of 3.8 $Å^2$. As it turned out the guess of 3.0 $Å^2$ for the B-factor of the copper atom was very poor, but the guess of 3.8 $Å^2$ was

surprisingly close to the mark for the oxygen atoms and some of the carbon atoms, The initial values of both atomic coordinates and thermal parameters are shown in Table 2.

Table 2

Atom	x	y	B(Å^2)
Cu	0.0000	0.0000	3.0
O_1	0.1348	-0.0176	3.8
O_2	0.0586	0.1328	3.8
C_1	0.2031	0.0488	3.8
C_2	0.1523	0.1387	3.8
C_3	0.2168	0.2207	3.8
C_4	0.3145	0.2539	3.8
C_5	0.3984	0.1992	3.8
C_6	0.3965	0.1016	3.8
C_7	0.3027	0.0391	3.8

Table 2: Values of parameters before refinement.
x and y are given in terms of fractions of the unit cell edges.

Table 3

Atom	x	y	B(Å^2)
Cu	0.0000	0.0000	4.0
O_1	0.1365	-0.2459	4.3
O_2	0.0571	0.1295	3.9
C_1	0.2054	0.0470	4.2
C_2	0.1564	0.1398	3.9
C_3	0.2141	0.2263	4.3
C_4	0.3156	0.2514	4.1
C_5	0.3974	0.1993	6.3
C_6	0.4005	0.1059	6.3
C_7	0.3074	0.0386	4.2

Table 3: Values of parameters after 11 cycles refinement using NYXRl.
x and y are given in terms of fractions of the unit cell edges.

To begin with an attempt was made to refine thermal parameters and atomic co-ordinates simultaneously. Seven cycles of refinement were carried out in this manner. However, the structure went into oscillation and this approach was abandoned after the seventh cycle. The nature of the oscillation is shown in Table 4. The values of various quantities are shown at the end of each cycle.

These quantities are:

a) $R = 100\sum||Fo| - |Fc|| / \sum|Fo|$. (Discrepancy).

b) $R' = \sum(|Fo| - |Fc|)^2$. (R prime).

c) Scale factor.

d) B- factor for the copper atom.

Table 4

Stage of refinement	R	R′	Scale	B(Å)^2
Input structure	22.0	3,588	1.0000	3.0
After 1 cycle	24.0	2,556	0.8262	3.2
After 2 cycles	16.9	2,259	0.9528	3.7
After 3 cycles	22.5	2,151	0.7911	3.6
After 4 cycles	15.8	2,116	0.9366	4.1
After 5 cycles	23.3	2,258	0.7597	3.9
After 6 cycles	16.4	2,301	0.9377	4.4
After 7 cycles	--	--	0.7345	4.2

It will be seen that B for copper first rose and then began to rise and fall. There was also a fluctuation in the R factor. When the B factor of copper increased, the scale factor also increased. After the fourth cycle R′ began to increase. The variation of the B factor for copper only is shown, but all the other parameters showed the same sort of fluctuation from cycle to cycle.

A structure can show this sort of behaviour during refinement if too few planes have been observed to determine all the parameters fully, or if the accuracy with which the intensities were measured was low in comparisom with the number of observed planes. It was assumed at the time these computations were performed that the explanation of the oscillation might be along these lines. Therefore, the atomic co-ordinates were then refined alone. After they had converged the thermal parameters were refined alone. Finally one further cycle of refinement was carried out on atomic coordinates alone. Separating atomic coordinates and thermal parameters during refinement reduced the number of variables at each stage and the parameters converged without oscillation.

The atomic co-ordinates converged after six cycles of refinement. During these six cycles the R-factor fell from 22.0 to 20.7 and R′fell from 3588 to 2312. This would indicate that the original choice of co-ordinates from the Fourier map was substantially correct. No large change in co-ordinates was observed.

Thereafter four cycles of refinement were carried out in which the B-factors were considered the only variables. At the end of these cycles the R-factor had dropped to 14.9, and R′ to 1,318. This showed that the lack of agreement between the observed structure factors and the structure factors calculated from the initial co-ordinates was due principally to the poor choice of thermal parameters for the atoms.

The final cycle of refinement carried out on atomic co-ordinates alone resulted in insignificant changes in atomic co-ordinates and in R. The atomic co-ordinates and isotropic thermal parameters obtained as a result of this analysis are listed in Table 3.

It will be noted that the R-factor of 14.9 for 154 observed planes was already less than the value of 15.8 for 112 planes reported for the previous analysis[2].

It will be further observed that C_5 and C_6 had much higher thermal parameters than the other atoms, and that these thermal parameters were equal. This meant that the amplitude of vibration of these atoms was much greater than that of the other atoms. Also it appeared that these atoms were vibrating as a unit. This deduction appeared to be at variance with the conception of the tropolone ring as a regular heptagon. This point will be discussed more fully later on.

Refinement of atomic co-ordinates and anisotropic thermal parameters

Strictly speaking, the assumption that the thermal vibration of the atoms in a molecule is isotropic can be justified in very few cases and then only when the atom has bonding which is symmetrical in three dimensions, e.g. the carbon atom in diamond. It is certainly not justified in the case of copper tropolone. Take the case of any carbon atom in that compound. It may be expected to execute vibrations of greater magnitude along lines which are not parallel to the bonds connecting it to other atoms, since these bonds will exercise a restraint upon the thermal vibrations.

Inspection of the contours on the Fourier map (Fig. 1) shows that the shapes of the atoms are elliptical in many cases, and not circular. This is further evidence for the existence of anisotropic thermal motion in the crystal. This reasoning seemed to justify the extension of the analysis to include the effects of anisotropic thermal vibrations.

The calculations were carried out on the I.B.M. 704 electronic computer. The parameters were refined using the method of least squares. The programme used was written for the purpose of refining this structure, but was written as a general programme for the least squares refinement in three dimensions of the structure of a molecule in any centro-symmetric space-group (Appendix III).

Before beginning this stage of the refinement reasonable positions were found for the hydrogen atoms. The data used were the final co-ordinates of the carbon atoms from the previous refinement (Table 3), the inclination of the ring published previously[2], and the value of the carbon to hydrogen bond found in sodium tropolone[4]. The hydrogen atoms were then given the isotropic temperature factor of the carbon atoms to which they were attached. The parameters of the hydrogen atoms were not refined, but were included in the structure

factor calculations. These parameters are shown in Table 5.

Since the structure had gone into oscillation when the atomic co-ordinates and the isotropic thermal parameters were refined simultaneously, it was decided to refine atomic co-ordinates and anisotropic thermal parameters separately. However the procedure adopted was different. Seven cycles of refinement were carried out, atomic co-ordinates and thermal parameters being adjusted alternately. In all, four cycles of refinement were carried out on the atomic co-ordinates; between each of these cycles a cycle of refinement on thermal parameters alone was carried out.

During the last cycle on thermal parameters the thermal parameters changed by an average amount of 3×10^{-4}. During the final cycle, the atomic co-ordinates changed by an average amount of 0.001. Over these two cycles R remained at 12.2% and R′ at 810. At this point it was considered that the structure had converged, and that further refinement would be of no advantage.

The final atomic co-ordinates and thermal parameters are given in Table 5. In Table 5 there are two columns

labelled B_α and B_β. These are the anisotropic thermal parameters expressed in the more familiar Debye-Waller units.

$$B_\alpha = 4\alpha/a^{*2}.$$

$$B_\beta = 4\beta/b^{*2}.$$

$\sigma(x)$ and $\sigma(y)$ are the standard deviations of the atomic co-ordinates calculated by Cruickshank's formula[19].

The structure factors calculated using these data (F_c) are listed in Table 6, together with the observed structure factors (F_o). The observed structure factors were placed as nearly as possible on an absolute basis by including the scale factor as one of the parameters. In all structure factor calculations the atomic scattering curves used were those evaluated by Berghuis et al[18].

Table 5

Atom	x	$\sigma(x)$	y	$\sigma(y)$	$\alpha(\times 10^2)$	$\beta(\times 10^2)$	$B\alpha(Å^2)$	$B\beta(Å^2)$
Cu	0.0000	0.0000	0.0000	0.0000	0.8977	0.5309	4.8	4.1
O_1	0.1342	0.0012	-0.0249	0.0016	1.0716	0.5655	5.7	4.3
O_2	0.0564	0.0011	0.1291	0.0015	0.8938	0.4435	4.8	3.4
C_1	0.2037	0.0017	0.0505	0.0022	1.1355	0.4998	6.1	3.8
C_2	0.1562	0.0016	0.1371	0.0021	1.1976	0.3871	6.4	3.0
C_3	0.2120	0.0017	0.2292	0.0022	1.0132	0.7732	5.4	5.9
C_4	0.3135	0.0018	0.2612	0.0023	1.0648	1.4279	5.7	10.9
C_5	0.4030	0.0018	0.1991	0.0023	1.6492	0.8763	8.8	6.7
C_6	0.3973	0.0020	0.1060	0.0027	1.3459	0.9407	7.2	7.2
C_7	0.3064	0.0016	0.0393	0.0021	0.7538	1.0493	4.0	8.0
H_3	0.1712		0.2814				4.3	
H_4	0.3379		0.2486				4.1	
H_5	0.4710		0.2405				6.3	
H_6	0.4793		0.0832				6.3	
H_7	0.3172		-0.0289				4.2	

Final values of atomic coordinates and thermal parameters. The atomic coordinates are given in units of fractions of the unit cell edges.

Table 6

Observed structure factors and structure factors calculated using coordinates in Table 5.

Plane	Fo	Fc	Fo − Fc
200	5.3	6.4	- 1.1
400	8.9	8.1	0.8
600	40.2	35.6	4.6
800	7.0	4.2	2.8
10,0,0	13.6	15.3	- 1.7
12,0,0	3.7	1.2	2.5
14,0,0	4.7	4.2	0.5
020	53.3	50.3	3.0
040	52.3	60.6	- 8.3
060	30.5	28.7	1.8
080	44.3	46.4	- 2.1
0,10,0	4.4	8.3	- 3.9
0,12,0	- 3.2	- 2.9	- 0.3
0,14,0	8.3	8.2	0.1
0,16,0	5.8	6.8	- 1.0
110	74.6	73.1	1.5
120	-53.5	-61.7	8.2

Table 6 (contd.)

Plane	Fo	Fc	Fo - Fc
130	49.4	47.3	2.1
140	- 4.7	- 3.2	- 1.5
150	30.9	33.9	- 3.0
160	6.0	3.9	2.1
170	58.4	53.4	5.0
180	5.8	3.0	2.8
190	25.7	24.2	1.5
1,10,0	- 8.0	- 4.7	- 3.3
1,11,0	6.8	2.6	4.2
1,12,0	8.9	8.6	0.3
1,13,0	10.9	9.7	1.2
1,14,0	5.4	6.7	- 1.3
1,15,0	8.7	9.2	- 0.5
1,17,0	3.8	3.9	- 0.1
210	6.2	12.3	- 6.1
220	44.2	42.5	1.7
230	-12.3	- 8.4	- 4.4
240	- 5.2	- 5.6	0.4
250	34.5	34.3	0.2
260	40.0	41.9	- 1.9

Table 6 (contd.)

Plane	Fo	Fc	Fo - Fc
270	10.0	14.0	4.0
280	30.1	30.8	- 0.7
290	- 3.0	- 5.5	2.5
2,10,0	27.3	26.8	0.5
2,11,0	9.4	8.2	1.2
2,12,0	10.2	11.7	- 1.5
2,13,0	9.0	11.2	- 2.2
2,14,0	9.2	8.7	0.6
2,16,0	6.1	6.6	- 0.5
310	33.1	28.1	5.0
320	- 29.9	-31.2	1.3
330	30.7	32.7	- 2.0
340	22.1	22.7	- 0.6
350	20.0	20.7	- 0.7
360	33.0	31.5	1.5
370	22.4	26.4	- 4.0
380	13.0	10.3	2.7
390	16.6	19.6	- 3.0
3,10,0	- 2.3	- 1.4	- 0.9
3,11,0	20.2	19.7	0.5

Table 6 (contd.)

Plane	Fo	Fc	Fo - Fc
3,13,0	7.4	6.5	0.9
3,14,0	3.4	4.6	- 1.2
3,15,0	7.6	6.3	1.4
3,17,0	3.0	4.5	- 1.5
410	7.5	3.2	4.4
420	23.7	25.2	- 1.5
430	- 4.2	- 5.0	0.8
440	36.6	35.1	1.5
450	5.7	3.4	2.3
460	15.2	15.4	- 0.2
470	3.8	3.2	0.6
480	18.7	15.3	3.4
490	-10.6	- 9.0	- 1.6
4,10,0	13.3	10.3	3.0
4,11,0	- 1.8	- 2.7	0.9
4,12,0	5.6	12.0	- 6.4
4,14,0	7.7	7.0	0.7
4,16,0	4.6	5.2	- 0.6
510	32.6	33.3	- 0.7
520	-17.2	-13.1	- 4.1

Table 6 (contd.)

Plane	Fo	Fc	Fo - Fc
530	6.6	9.2	- 2.6
540	- 6.2	- 4.2	- 2.0
550	24.4	25.5	- 1.1
560	- 7.2	- 5.6	- 1.6
570	7.6	7.7	- 0.1
580	- 4.9	- 2.3	- 2.6
590	17.2	18.9	- 1.7
5,10,0	- 4.9	- 8.3	3.4
5,11,0	8.8	8.8	0.0
5,13,0	10.1	8.0	2.1
5,15,0	2.7	5.0	- 2.3
610	-14.3	-16.1	1.8
620	31.1	32.5	- 1.4
630	- 7.9	-11.4	3.5
640	37.0	36.3	0.7
650	- 4.5	- 2.9	- 1.6
660	18.6	20.4	- 1.8
680	15.8	16.4	- 0.6
690	- 5.9	- 5.5	- 0.4
6,10,0	2.3	4.8	- 2.5

Table 6 (contd.)

Plane	Fo	Fc	Fo - Fc
6,11,0	- 6.8	- 5.3	- 1.5
6,12,0	9.6	8.0	1.6
6,14,0	4.0	5.7	- 1.7
6,16,0	4.0	2.5	1.5
710	21.8	28.1	- 6.3
720	- 4.2	- 6.4	2.2
730	34.2	30.1	3.3
740	- 8.2	- 8.2	0.0
750	22.3	23.6	- 1.3
770	18.1	19.8	- 1.7
780	- 9.8	- 9.4	- 0.4
790	9.0	9.3	- 0.3
7,10,0	- 3.6	- 4.5	0.9
7,11,0	12.8	11.1	1.7
7,13,0	3.9	4.6	- 0.7
810	- 7.3	- 3.6	- 3.7
820	19.2	22.6	- 3.4
830	- 5.6	- 6.0	0.4
840	15.3	17.3	- 2.0
850	11.8	11.5	0.3

Table 6 (contd.)

Plane	Fo	Fc	Fo - Fc
860	18.3	17.5	0.8
880	9.2	8.0	1.2
8.10,0	13.3	12.6	0.7
8,12,0	7.8	8.6	- 0.8
8,14,0	3.3	2.9	0.4
910	9.1	9.5	- 0.4
920	8.3	5.5	2.8
930	23.2	22.7	0.5
940	7.4	7.2	0.2
950	17.2	18.0	- 0.8
960	9.9	9.1	0.8
970	2.9	3.4	- 0.5
980	4.7	3.6	1.1
990	5.4	4.5	0.9
9,11,0	7.5	6.6	0.9
9,13,0	4.2	4.8	- 0.6
10,1,0	- 2.9	- 1.7	- 1.2
10,2,0	9.1	10.0	- 0.9
10,3,0	5.4	5.3	0.1

Table 6 (contd.)

Plane	Fo	Fc	Fo - Fc
10,4,0	16.3	17.3	- 1.0
10,10,0	6.5	4.9	1.6
10,12,0	3.9	4.2	- 0.3
11,3,0	7.3	7.2	0.1
11,4,0	- 2.5	- 2.9	0.4
11,5,0	6.4	6.0	0.4
11,6,0	- 6.7	- 6.1	- 0.6
11,7,0	4.2	3.8	0.4
11,11,0	4.5	4.9	- 0.4
12,1,0	7.8	5.5	2.3
12,6,0	5.3	5.1	0.2
13,1,0	6.3	6.3	0.0
13,3,0	2.8	4.5	- 1.7
13,5,0	3.1	3.5	- 0.4
13.7.0	4.5	3.9	0.6
14,2,0	4.8	3.6	1.2
14,4,0	3.4	3.2	0.2
14,6,0	1.6	2.8	- 1.2

Derivation of bond lengths

If the tropolone ring in copper tropolone is a planar regular heptagon then its projection on the hk0 plane should be an ellipse. If the major axis of the ellipse is m and the minor axis is n then the inclination of the tropolone ring to the projection plane, θ, is given by the relation:

$$\cos\theta = n/m.$$

The direction of maximum inclination of the ring is parallel to n, and lines parallel to m will have zero inclination. In any other direction making an angle, ζ, with the direction of n, the angle ψ between a line in the molecular plane and its projection will be given by the relation:

$$\tan\psi = \tan\theta\cos\zeta.$$

The true length, R, of a line in the molecular plane whose projection has a length, r, is then given by:

$$R = r/\cos\psi.$$

The bond lengths previously reported for copper tropolone[2] were derived on this basis. It should be noted that to apply the above reasoning it is not

essential that the ring be a regular ring, but that it need only be planar. Where the ring is not regular it can be treated as approximately regular. The ellipse which most closely fits the points in projection can then be found by a least squares treatment. The ratio of the minor to the major axes of this ellipse will then give the inclination of the ring as before.

Fitting of ellipse

The ellipse was fitted to the projected atoms by the method of least squares. Five parameters were required to define the ellipse. The coordinates of seven atoms lying approximately on the ellipse were available to define these parameters. The parameters of the ellipse were:

(ξ_o, η_o) : coordinates of the centre of the ellipse with respect to the projection axes, a and b.

m : major axis of ellipse

n : minor axis of ellipse

α : inclination of m to the a axis in the projection.

Now, if (ξ, η) are the co-ordinates of any point on the ellipse with respect the centre of the ellipse, then:

$$\xi^2 / m^2 + \eta^2 / n^2 = 1 \quad \ldots\ldots\ldots (2)$$

It can be shown that if (x, y) are the coordinates with respect to the projection axes of the point (ξ, η), then:

$$\xi = (y - \eta_o) \cos \alpha - (x - \xi_o) \sin \alpha$$

$$\eta = (x - \xi_o) \cos \alpha - (y - \eta_o) \sin \alpha$$

By substituting these values of ξ and η in the equation of the ellipse we obtain the equation for the ellipse with respect to the projection axes.

In the least squares fitting of the ellipse the values of α, m and n published by Robertson[2] were taken as the initial values; the coordinates of the centre of the ellipse (ξ_o, η_o) were estimated from the projection. The coordinates of the seven carbon atoms on the ring gave seven conditional equations from which the five normal equations were derived. The formulae for the partial differentials used are rather complicated, but may be readily derived by differentiating the equation of the ellipse.

The final parameters of the ellipse are given below:

$$\xi_o = 0.288 \text{ a}$$

$$\eta_o = 0.142 \text{ b}$$

$$\alpha = 65^\circ\ 26'$$

$$m = 1.60 \text{ Å}$$

$$n = 1.43 \text{ Å}$$

The maximum inclination of the ring was now 27° 45′.

Bond lengths

The bond lengths in copper tropolone, derived by the method outlined in the previous section, are shown in Table 7 in the column headed L_m. In the column headed L_R the bond lengths obtained in the previous investigation are listed for comparison.

Table 7

Bond	L_m (Å)	L_R (Å)
Cu - O_1	1.76	1.83
Cu - O_2	1.92	1.98
O_1 - C_1	1.32	1.34
O_2 - C_2	1.28	1.25
C_1 - C_2	1.43	1.41
C_2 - C_3	1.44	1.37
C_3 - C_4	1.31	1.39
C_4 - C_5	1.49	1.45
C_5 - C_6	1.33	1.39
C_6 - C_7	1.44	1.41
C_7 - C_1	1.32	1.38

No estimate of the accuracy of these bond-lengths was made.

Discussion

In the previous analysis a marked alternation in C - C bond lengths around the ring was observed. The average bond length was 1.41 Å. However, with an estimated standard deviation in bond-lengths of 0.03 Å, the data were consistent with the concept of the tropolone ring as a planar, regular heptagon of side 1.41 Å. It was expected that a refinement of this analysis would reduce the differences in length of the bonds around the ring.

In fact, the refinement produced exactly the opposite effect. Refinement of the structure emphasized the alternation in bond length around the ring. Therefore this present analysis suggests that, in copper tropolone, the tropolone ring is not a regular heptagon. Some of the bonds more nearly approach single bond character (e.g. $C_4 - C_5$), while others more closely approach a double bond character (e.g. $C_5 - C_6$).

The bond lengths around the ring were calculated on the assumption that the ring was planar; it was unnecessary to assume that the ring was a regular heptagon. If the ring is planar then these bond lengths should be fairly accurate. If these bond lengths are

accurate then it is difficult to explain why the short bonds ($C_3 - C_4$, $C_5 - C_6$, $C_7 - C_1$) have lengths almost exactly equal to the accepted value for an ethylenic double bond (1.33 Å), while the other longer bonds have lengths much shorter than the accepted value for a pure C - C single bond (1.54 Å). It is to be expected that if the short bonds are pure double bonds then the long bonds should be pure single bonds. That this should not be true casts doubt on the accuracy of the bond lengths listed in Table 7. Therefore if the bond lengths are not acceptable the assumption made in their calculation must be wrong. In other words the ring is not planar.

Now if the ring is not a regular planar heptagon then certain features observed in the bond lengths become easier to explain. If the ring is puckered slightly then it will be impossible to predict the inclination to the projection plane of any bond from two dimensional data alone. Some bonds may well be inclined to the plane of projection at an angle greater than the maximum inclination of c.28° as calculated in a previous section. The values of the bond lengths calculated for such bonds will be less than their true values. This is almost

certainly the case with the bond $C_3 - C_4$ which, with a length of 1.31 Å, appears to be shorter than a pure double bond.

On the other hand some bonds might be inclined to the projection plane at smaller angles than would be the case if the ring were planar. The lengths calculated for these bonds would be greater than their true values. This would explain the comparatively long bond between C_4 and C_5. This bond appeared comparatively long in the previous analysis also[2].

If the tropolone rings were of the regular planar aromatic type it would be expected that the thermal vibrations in the plane of the ring would be of small amplitude compared with those perpendicular to the ring. Most of the thermal motion of the atoms in the plane of the ring would be due to vibration of the molecules as a whole about an axis perpendicular to the ring through the copper atom. In this case the thermal motion should show two features:

a) the atoms farthest from the copper atom should have the largest B values, and

b) the ratio of $B\alpha$ to $B\beta$ should not vary much from one atom to the other.

Inspection of Table 5 shows that the largest B value is that of 10.9 assigned to C_4, which is not quite the most distant of the carbon atoms from the copper atom. Still all the carbon atoms have fairly high thermal parameters and so it is difficult to draw any conclusion from the magnitude of the B-factors alone. The ratio $B\alpha/B\beta$ varies from 0.5 in C_4 and in C_7 to 2.1 in C_2, and the change in ratio from atom to atom follows no simple rule. Thus each atom seems to have a well defined mode of vibration of its own.

While no hard and fast conclusion can be drawn from these qualitative remarks on the thermal motion of the atoms, the observed anisotropic thermal parameters seem to be more in agreement with the view of the ring as an irregular, slightly puckered structure.

Comparison with Sodium Tropolone

The bond lengths in the tropolone ring in sodium tropolone[4] were found to alternate around the ring in the same way as in copper tropolone. The authors detected a slight deviation from planarity in the ring, but they were uncertain whether or not this deviation was significant. In the absence of definite information

about the bond lengths in copper tropolone it is not possible to make a direct comparison of the two salts. However the following observations may be made.

Sodium tropolone is a largely ionic compound and the tropolone ring exists as the anion $(C_7H_5O_2)^-$. In this the structures II mentioned in the Introduction are the dominant contributors to the final hybrid, and the bonding electrons tend to be distributed uniformly around the ring. The observed variation in bond lengths can be ascribed to the contribution of structures other than II.

As far as can be judged from the (hk0) projection the copper atom in copper tropolone is bonded to all four oxygen atoms in the two tropolone rings associated with it. In order to accomplish this the copper atom must be hybridised in the dsp^2 state. These hybridised bonds are covalent and the electrons forming them must be largely localised between the copper and the oxygen atoms. In sodium tropolone these electrons are not restricted to the same extent to any particular location or atom in the ring, and the resulting delocalisation energy stabilises the ring into a planar aromatic-type heptagon. In copper tropolone this delocalisation energy cannot be nearly so

large. As a result the tropolone ring in copper tropolone will not have so much aromatic character as in sodium tropolone. Still more alternation in bond lengths around the ring might then be expected in copper tropolone, and the ring need not be planar.

Conclusion

This analysis suggests that in copper tropolone the tropolone ring is not a regular heptagon and is non-planar. In the absence of three dimensial data it has not been possible to obtain the bond lengths around the ring, or to interpret fully the thermal motion of the atoms.

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CRYSTAL AND MOLECULAR STRUCTURE OF COPPER NOOTKATIN

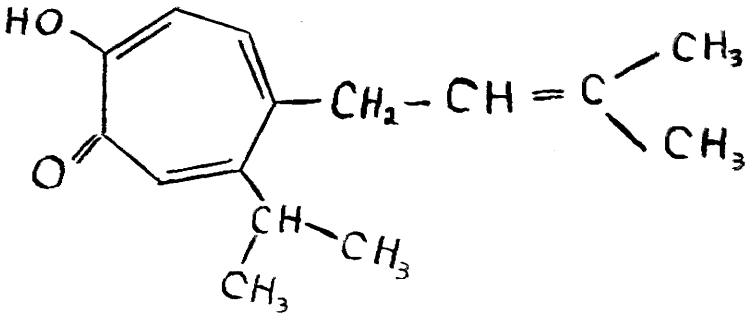
INTRODUCTION

Nootkatin was isolated in 1950[1] from the heartwoods of the yellow cypress, the yellow cedar and the Alaska cedar. These woods are remarkable for their resistance to fungus growths, particularly dry rot. The antifungal agent was shown by Erdtmann[1] to be nootkatin. Thus nootkatin might acquire commercial importance as a fungacide.

The formula of nootkatin was found to be $C_{15}H_{20}O_2$[1]. Its ultra-violet and infra-red absorption spectra indicate that it is a tropolone derivative[1]. It was shown to have two aliphatic side-chains, isopropyl and 2-methyl-but-2-enyl,[1] but at the time of publication of this information the positions of the substituents in the tropolone ring had not been established.

Accordingly, an investigation of the structure of the copper salt was undertaken in this department by R.B. Campbell[2]. The copper derivative was chosen in order to make use of the phase determining power of the heavy copper atom to determine the structure directly. Unfortunately, Campbell's analysis was confined to the (0kl) zone of reflexions since the shape of the crystals

was unsuitable for the examination of any other. Now, in this zone, and in the (hko) zone, the copper atoms make a contribution only to those planes for which k + l or h + k is even[2]. Consequently an element of trial and error entered into Campbell's analysis. The structure found was:



This present investigation was undertaken with a view to extending the analysis to the (hol) zone in which the copper atoms contribute to all of the planes, and so determines their relative phases. Such an analysis is therefore completely direct, and independent of any chemical assumptions. The visual estimation of the intensities in the (hol) zone, and the checking of the crystal constants and unit cell dimensions were carried out by this writer at an earlier time[3]. This present report will describe the verification of Campbell's

structure only.

Shortly after this work was begun, Campbell's structure was confirmed chemically by Erdtmann[4].

CRYSTAL DATA

Formula:	$C_{30}H_{38}O_4Cu$
Molecular Weight:	526.2
Monoclinic:	$a = 8.40$ Å $b = 11.96$ Å $c = 15.21$ Å
	$a^* = 0.2031$ $b^* = 0.1287$ $c^* = 0.1122$
	$\beta = 115.5°$
Absent spectra:	(hol), when h is odd
	(0k0), when k is odd
Space group:	$C^5_{2h} - P2_1/a$
$d_{obs} = 1.27$	$d_{calc} = 1.256$

Two molecules per unit cell.

Volume of unit cell = 1,391 $Å^3$

Absorption coefficient for X-rays ($\lambda = 1.542$ Å) = 14.7 $cm.^{-1}$

Total number of electrons in unit cell (F[000]) = 558

Refractive index along a = 1.619

Refractive index along b > 1.87

Refractive index along c - not measured owing to unsuitable shape of crystals.

ANALYSIS OF STRUCTURE

A two-dimensional Fourier synthesis had been performed on the (hol) zone reflexions measured previously[3]. The synthesis was carried out by summing the function:

$$p(x,z) = \frac{1}{A}\sum\sum F(hol)\ \cos 2\pi(hx + lz)$$

The signs of all the structure factors were assumed to be +. The summation was carried out on a desk calculator with the aid of Robertson-Tunell strips and stencils. Now although it was very reasonable to assume that the copper atoms determined the phases of all the important planes, and that the Fourier synthesis gave, therefore, a fairly exact representation of the molecule in projection, none of the atoms was resolved in the resulting map.

Lines were drawn across the map parallel to the a-axis and cutting the c-axis at points corresponding to the z-coordinates of the atoms determined by Campbell. Thus, it seemed reasonable to suppose that the atoms lay somewhere on these lines. However, it was not possible to assign x-coordinates to the atoms with any great accuracy even with this information at hand. Along each line were regions of high electron density at any point of

which a carbon or oxygen atom might easily be placed. Several sets of positions were chosen, each of which seemed resonable from the expected configuration of the molecule. On calculation of structure factors however, these sets of coordinates gave residuals of between 36% and 49%, and none appeared worth further consideration.

A new approach was tried. A model of the structure was constructed from wood and wire. On a heavy 5-ply wood base were plotted the positions of the atoms with respect to the orthogonal b and c axes, using the coordinates obtained by Campbell. In a plane at right angles to the base, and parallel to the c axis, holes were drilled at an angle of 64.5° to the base. Straight wires were inserted in these holes. These wires correspond to lines through the atoms parallel to the a-axis.

Using the bond lengths reported in copper tropolone[5], and the values for carbon to carbon single and double bonds reported elsewhere[6], the positions of the atoms on the wires were established. The various atoms were simply set at the reported distances in space from one another. The distance of any atom from the base, as measured along the wire carrying it, was a measure of the x-coordinate of that atom. The scale of the model

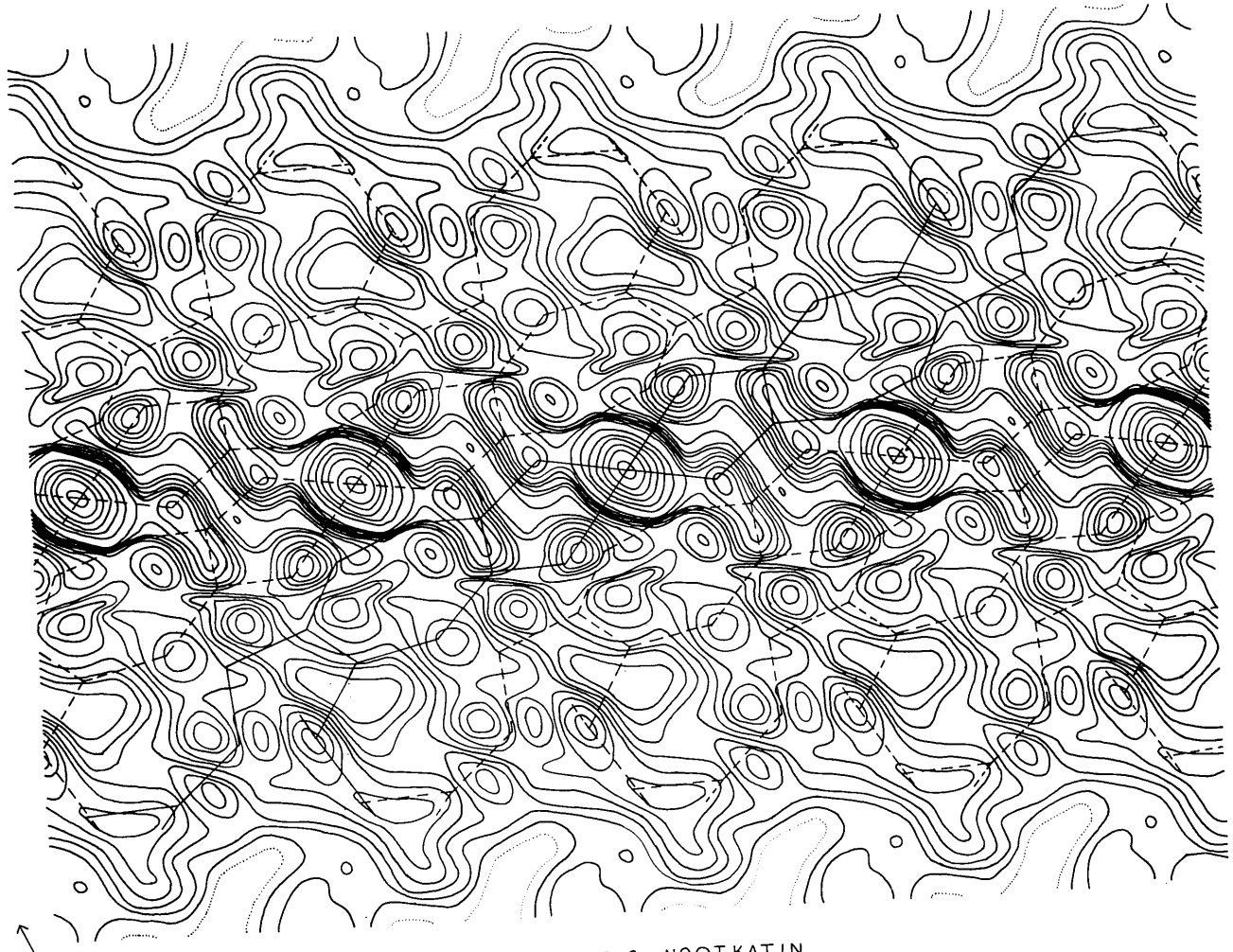


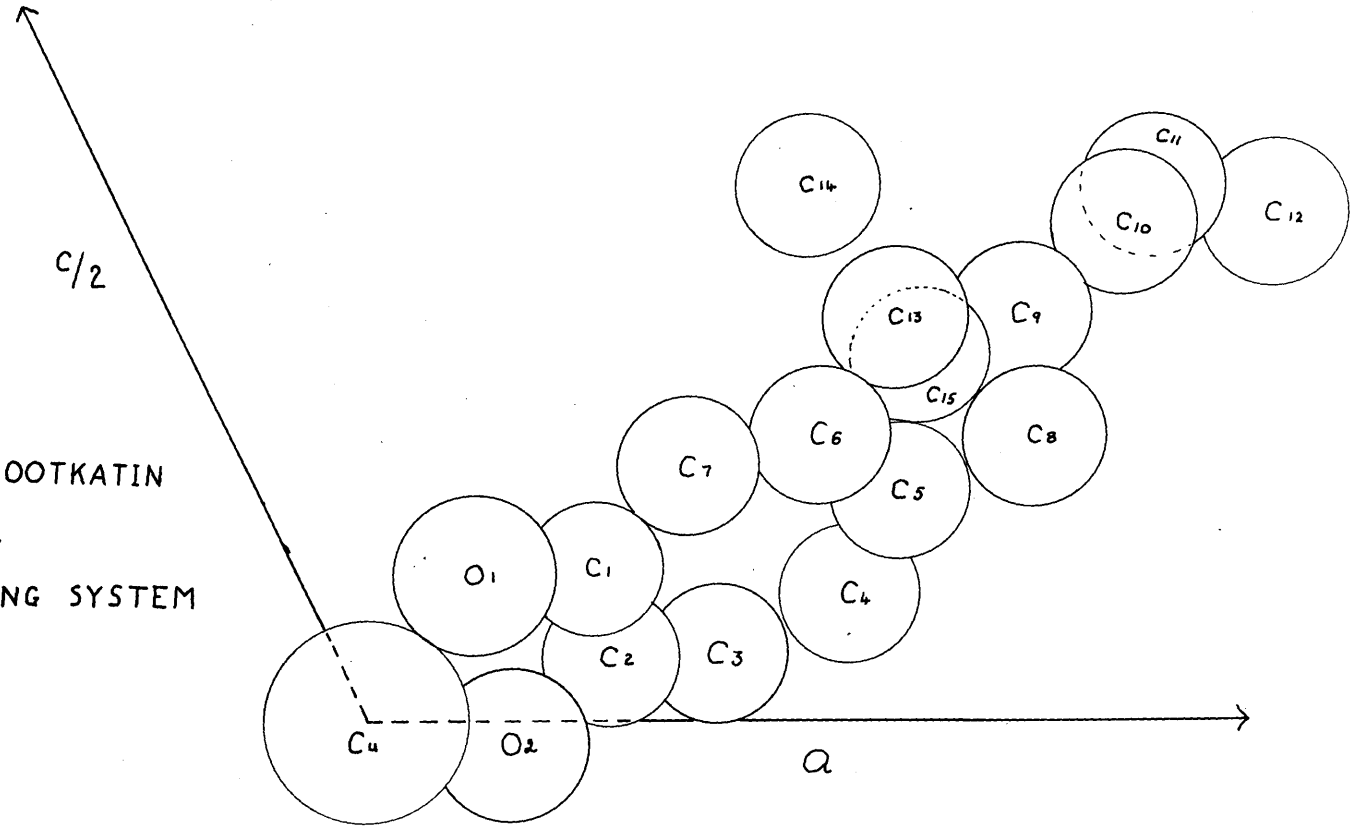
Fig. 1. CUPRIC NOOTKATIN

(h0ℓ) PROJECTION SHOWING MOLECULE (FULL LINES) AND ADJACENT MOLECULES (BROKEN LINES)

CUPRIC NOOTKATIN

FIG. 2.

ATOM NUMBERING SYSTEM



was such that 1 Å was represented by 5 cm.

In this model the tropolone ring turned out to be planar within the limits of measurement. The normal from the plane of the tropolone ring made an angle of 61° with the direction of the a-axis, which is in good agreement with Campbell's calculated value of 65.9°[2].

The x-coordinates obtained from the model are shown below in Table 1, together with the y- and z-coordinates obtained from Campbell's analysis. The structure factors calculated for the (hol) zone using Campbell's z-coordinates appear in Table 2. The discrepancy between the calculated and observed values over the 44 planes (excluding 00 l reflexions) is 19%. In Fig. 1 is shown the revised Fourier map which is obtained when the two changes in sign are included in the calculation. Fig. 2 identifies the atoms listed in Table 1.

TABLE 1

Coordinates of the atoms expressed as fractions of the unit cell edges

x-coordinates - Macintyre.

y- and z-coordinates - Campbell[2].

Atom	x	y	z
Cu	0.000	0.000	0.000
O_1	0.203	-0.064	0.102
O_2	0.151	0.098	-0.014
C_1	0.340	-0.012	0.107
C_2	0.310	0.081	0.045
C_3	0.431	0.157	0.034
C_4	0.613	0.158	0.087
C_5	0.716	0.083	0.160
C_6	0.667	-0.007	0.201
C_7	0.500	-0.486	0.179
C_8	0.910	0.107	0.201
C_9	0.956	0.166	0.286
C_{10}	0.112	0.145	0.350
C_{11}	0.117	0.222	0.431
C_{12}	0.305	0.044	0.356
C_{13}	0.815	-0.068	0.282
C_{14}	0.785	-0.054	0.376
C_{15}	0.823	-0.187	0.259

TABLE 2

Structure factors calculated using coordinates of Table 1

Plane	$F_{obs.}$	$F_{calc.}$	Plane	$F_{obs.}$	$F_{calc.}$
20,10	22	21	403	23	29
209	28	34	402	26	37
208	38	31	401	20	25
207	36	32	400	39	32
206	50	49	$40\bar{1}$	24	18
205	60	49	$40\bar{2}$	22	-12
204	82	82	$40\bar{4}$	43	55
203	8	8	$40\bar{5}$	47	45
202	15	20	$40\bar{6}$	40	49
201	74	62	$40\bar{7}$	28	24
200	59	48	604	23	27
$20\bar{1}$	37	30	603	19	12
$20\bar{2}$	27	40	601	30	37
$20\bar{3}$	40	45	600	42	41
$20\bar{4}$	55	40	$60\bar{1}$	32	23
$20\bar{5}$	21	26	$60\bar{2}$	27	43
$20\bar{6}$	43	44	$60\bar{3}$	34	29
$20\bar{7}$	26	30	$60\bar{4}$	18	9
$20\bar{8}$	35	-27	$60\bar{9}$	12	18
407	31	33	$60,\bar{10}$	29	43
406	22	20	$60,\bar{11}$	31	30

$\sum |F_{calc}| = 1,409$ $\quad\quad$ $\sum ||F_{obs.}| - |F_{calc.}|| = 267$

% Discrepancy $= 100 \times \sum ||F_{obs}| - |F_{calc}|| / \sum |F\ calc| = 19\%$

DISCUSSION

In the (okl) zone, Campbell's coordinates gave the overall discrepancy of 22%. In the calculation of the structure factors in this zone, he used an empirical scattering curve for the copper atom[2], and empirical curves for oxygen and carbon derived by Robertson[2]. In the present work the same scattering factors were used, and so the results should be strictly comparable.

Over 44 structure factors in which the x-coordinates of the atoms are involved a discrepancy of 19% indicates that the x-coordinates have not been determined too accurately. The coordinates are inaccurate because a fairly crude method had to be employed to derive them, viz., from a mechanical model. Further, these coordinates cannot be refined with the data available. In the (hol) zone there are 34 parameters (excluding temperature parameters) and 44 independent observed reflexions (or 55 reflexions if 00l reflexions are included). The accuracy with which the intensities were measured is probably not sufficiently high to warrant application of refinement procedures under these conditions.

None the less it should be borne in mind that x-coordinates were derived partly from Campbell's y- and z-coordinates, and partly from well established bond-lengths.

It is felt that the measure of agreement obtained between calculated and observed structure factors indicates that the choice of coordinates in the partially phase-determined (okl) zone was substantially correct.

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UNIT CELL DIMENSIONS AND SPACE, GROUP OF 2-METHOXY-6-METHYL-TROPONE

With the exception of the recent electron diffraction work carried out on tropone[1], no structural determination has been carried out on a tropolone without the presence of a heavy atom in the molecule. In an effort to remedy this situation 2-methoxy-6-methyl-tropone was selected for study. Tropolone itself had been rejected after a preliminary investigation[2]. The methyl ethers of tropolone are liquids at room temperature. This methyl-substituted tropolone methyl ether was the simplest tropolone available which was crystalline at room temperature. β-Methyl tropolone is also crystalline at room temperature, but is very difficult to obtain pure; it absorbs water vapor very readily to give a hemihydrate.

The sample of 2-methoxy-6-methyl tropone was very kindly supplied by Professor Haworth of Sheffield University.

CRYSTAL DATA

Molecular formula:	$C_9H_{10}O_2$
Molecular weight:	150
Melting point:	96° - 97°C
Crystal habit:	Long needles and a few plates. Marked cleavage along the needle axis.

Monoclinic: $\underline{a} = 7.69$ Å $\quad b = 6.23$ Å $\quad c = 8.32$ Å,

$\beta = 93.5°$

Absent spectra: 0k0 when k is odd

Space group: $C_2^2 - P2_1$

$d_{obs} = 1.270 \qquad d_{calc} = 1.253$

Two molecules per unit cell.

Molecular symmetry: none

Volume of unit cell: $398 Å^3$

All photographs taken with CuKα radiation, $\lambda = 1.542$ Å.

Rotation and oscillation photographs were taken about the $\underline{a}$ and $\underline{b}$ axes, and a rotation photograph was taken about the $\underline{c}$ axis. Multiple film (5 films) Weissenberg photographs were taken about the $\underline{a}$ and $\underline{b}$ axes, and a single film Weissenberg photograph was taken about the $\underline{c}$ axis.

The density of the crystals was found by the method of floatation. A mixture of bromo benzene (d = 1.499 g./c.c.) and a silicone fluid (density = c. 1.0 g./c.c.) was used. The silicone fluid was Hopkin and Williams MS 200/20. The density of the final mixture in which a crystal showed zero weight was determined using a pyknometer.

DISCUSSION

The study of this crystal was pursued no further than the space group determination. This compound is hygroscopic, and all photographs had to be taken with the crystal enclosed in a gelatin capsule. The moving film photographs show no strong high order reflexions which would help to establish a trial structure, and in all zones the number of reflexions observed was very much smaller than the total possible number. Attempts to increase the number of reflexions observed by increasing the exposure time failed. During the longer exposures the crystal tended to disintegrate giving a powder pattern. This powder pattern on the moving film photographs appeared as background radiation. The disintegration of the crystal was probably due to absorption of water vapor.

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APPENDIX II

IBM 704 Electronic Digital Computer

The computer is fully described in the accompanying manual (IBM 704 Programmers' Reference Manual, IBM Corp., New York, U.S.A., 1956).

The IBM 704 is a high speed machine with a basic machine cycle of 12 micro-seconds. Most instructions are executed in two cycles, but the computer is wired in such a way that the second cycle of one instruction overlaps the first cycle of the next. Thus in practice one instruction is carried out every 12 microseconds.

The memory of the machine is very extensive. It has three parts.

a) Primary storage

This consists of up to 32,768 binary words each of 36 bits. This is the high-speed memory, with an access time of less than one microsecond. The high speed of the machine is largely due to the choice of magnetic cores as primary storage.

b) Magnetic drum storage

Two magnetic drums are provided with a combined capacity of 8,192 binary words of 36 bits each.

c) Magnetic tape

Information can be stored on magnetic tapes. Each tape can carry up to 900,000 binary words of 36 bits.

Ten tapes may be used simultaneously.

The calculations are carried out using data already in the primary storage. The magnetic drums and tapes are used to store information for which there is no room in core storage. The tapes may also be used as input-output media. A useful feature of the computer is that calculations can be carried out and information read in from secondary storage simultaneously; these calculations need not be connected with the material being read in.

The IBM 704 computer has many features which make it a popular computer in the U.S.A. One of these is the provision of floating point instructions. Another is the provision of index registers which makes the programming of iterative procedures very simple.

APPENDIX III

LEAST SQUARES REFINEMENT OF CENTROSYMMETRIC STRUCTURES INCLUDING ANISOTROPIC THERMAL PARAMETERS

This program has been designed for the least squares refinement of anisotropic temperature parameters and atomic coordinates in a crystallographic analysis of molecular structure in centro-symmetric crystals. It can perform the following routines depending on the arrangement of sense switches on the computer:

a) calculation of structure factors only.

b) refinement of anisotropic temperature parameters and/or atomic coordinates.

c) the refinement is carried out using the diagonal terms of the least squares matrix alone.

d) the scale factor is treated as a variable. In the refinement all cross terms between scale factor and temperature parameters are included.
No cross terms between the scale factor and the atomic coordinates are included.

Mathematical Techniques

1) Evaluation of atomic scattering factors

The evaluation of the atomic scattering factors in the program is carried out by Vand's* method, in which

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* V. Vand, Acta Cryst., 10, p. 303 (1957).

the scattering factor is given the empirical representation:

$$f_\theta = A \exp(-a \sin^2\theta) + B \exp(-b \sin^2\theta) + C$$

A,a,B,b, and C are constants for each atom and these constants have been listed by Vand.

2) Evaluation of differentials

The form in which the structure factor is calculated is the following,

e.g. for PT:

$$F(hkl) = 2 \sum_{1}^{n} f_o \exp -(h^2\alpha_n + k^2\beta_n + l^2\gamma_n + hk\delta_n + kl\epsilon_n + hl\eta_n)$$

$$[\cos 2\pi(hx_n + ky_n + lz_n)]$$

Whenever possible the partial differentials are expressed in terms of the contribution of the particular atom concerned e.g., if fn(hkl) is the contribution of atom n to Fc(hkl), then

$$\frac{\partial F(hkl)}{\partial n} = -h^2 \, fn(hkl)$$

and similarly for the other variables. This means that calculation of differentials is very fast since the

quantity fn(hkl) must be calculated during the Fc(hkl) calculation in any case.

During the calculation of f(hkl) for one plane all the partial differentials of each atom with respect to that plane are evaluated. The appropriated cross products are then evaluated and added to a progressive sum. Therefore at the end of the structure factor routine all the coefficients of the normal equations are available in storage. If sense switch 1 is down (q.v.) then the differentials, cross products and sums are not computed. The structure factors only are calculated.

3) Solution of normal equations

The simultaneous equations obtained as in (2) are solved by an elimination method.

4) Scale factors

If $Z \sum|Fo| = \sum|Fc|$,

then Z is termed the scale factor.

This equation may be rewritten:

$$\sum|Fo| = 1/z \sum|Fc|$$

or

$$\sum|Fo| = (1-SC) \sum|Fc| \quad \ldots\ldots\ldots \quad (1)$$

where $Z = 1/(1-SC)$

i.e. $SC = 1 - 1/z$

As far as this program is concerned the scale factor is taken to be SC. The reason is that the refinement of scale factor can be carried out much more readily using an equation like (1).

INPUT-OUTPUT

The program at present is divided into two parts.

Part 1

This is a small program written to calculate the atomic scattering factors. Input to this program is thru two media, cards and tape. This part is kept separate from the main program to allow refinement of the same compound at different times without recalculation of the scattering factors.

Decimal Card Input

If there are K different chemical types of atom, then there will be (K + 3) IBM General Purpose Decimal Cards as input at this point.

The content of each card will be discussed in turn, and the order of the cards given is the order in which they must be read into the computer.

The card reading is carried out in accordance with the statement:

FORMAT (6E 10.4/12/14/ (5F 8.4))

For the meaning of this statement please consult "Fortran" Programmers' Manual.

Card 1 - 6E 10.4

Card 1 carries six crystal constants used in the evaluation of $\sin\theta$. Reading from left to right on the card, these are:

$\lambda^2 a^{*2}/4$, $\lambda^2 b^{*2}/4$, $\lambda^2 c^{*2}/4$, $\lambda^2 a^* b^* \cos\gamma^*/2$, $\lambda^2 b^* c^* \cos\alpha^*/2$, $\lambda^2 c^* a^* \cos\beta^*/2$.

λ = wave length of radiation used,

a^*, b^*, c^*, α^*, β^*, γ^* = reciprocal lattice constants of crystal as defined by James[1] (i.e. not including λ).

On the card each number is allotted ten columns. The numbers are expressed in floating point decimal form.

For example $\lambda^2 a^{*2}/4$ is punched columns 1-10 on the card, $\lambda^2 b^{*2}/4$ is punched in columns 11-20, and so on. The number might appear as:

0.9364E-02

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1. Crystalline State: Vol. II, James, page 598.

Card 2

Card 2 carries the number of chemically different types of atom in the asymmetric unit, in accordance with the format I2. Thus provision is made for a two-figure number of atoms. This number must be stored in columns 1 and 2 of the card. Also it must always be a two figure decimal integer e.g. 10, 05, 03 etc., but it should not exceed 10. If it does, then the entire program must be reassembled, with a new maximum value for this quantity listed in the DIMENSION statement.

Card 3

Card 3 carries the number of planes being considered according to format I4. This must be a four figure decimal integer punched in columns 1-4 of the card, e.g. 1000, 0154, 0024 etc.

Remaining cards

The remaining cards carry the constants required for the evaluation of the atomic scattering factor, viz., A,a,B,b, and C in that order according to format 5F8.4. Each constant is allotted eight columns on the card,

with four figures following the decimal point, e.g.

+ 09.6300

Each card carries the constants for one atom type only. Therefore, in general, there will be as many cards of this sort as there are chemically different atoms in the asymmetric unit.

These cards are arranged in the order given to the atoms they represent in the atom numbering system adopted for Program 2. e.g. Suppose we have $CuSO_4.H_2O$ and the numbering system is as follows:

Atom 1	Cu
Atom 2	S
Atom 3-7	O
Atom 8-9	H

Then the data would be distributed:

Card 4	Cu constants
Card 5	S constants
Card 6	O constants
Card 7	H constants

Provision is made in Program 2 for leaving certain atoms out of the refinement routine. This is possible since all inter-atom cross terms are ignored. This

is done by giving such atoms the first numbers in the list, and instructing Program 2 to begin refinement at the atoms following these. For example in the case of $CuSO_4.H_2O$, let us suppose that the parameters of the sulfate oxygen atoms are considered sufficiently well determined. The numbering would be as follows:

Atoms 1-4	O	Card 4
Atom 5	Cu	Card 5
Atom 6	S	Card 6
Atom 7	O	Card 7
Atoms 8-9	H	Card 8

It will be observed that the oxygen data are included twice. Program 2 is then instructed to commence refinement at atom 5.

BCD tape input

The reflexion data, h,k,l,W, and Fo, are fed into program 1 as BCD on tape No. 2. The data are read in one reflexion at a time, and after calculating the values of the atomic scattering factors, the program prints these values on Tape No. 3, together with h,K,l,W, and Fo. Tape 3 is a binary tape, and is the only output from Program 1. Thus although W and Fo are not required

by Program 1 it is useful to read them in with h,k and l and to have them converted to binary numbers on tape 3. The data for one plane make up one record on both tapes 2 and 3. Tape 3 is then used as input to Program 2.

Now the BCD information on tape 2 must be punched first on decimal cards. The cards are punched according to the statement:

FORMAT (3F5.1, F6.4, F8.2)

All information about any particular plane is contained on one card. Let us consider each of the fields in turn.

Miller Indices

The Miller indices of the plane are punched in columns 1-15 of the card, in the order h: 1-5, K: 6-10, l: 11-15. They are entered as a signed fixed point decimal quantities, with one digit after the decimal point in order that the computer will automatically convert them to floating point quantities, e.g.

+ 11.0

For a complete example see below.

Weighting factor-W

W is allotted 6 columns, running from 16-21. It is punched as an unsigned fixed point decimal with four digits after the decimal point: e.g. 0.5000.

Observed structure factor - Fo

On the card, Fo is allotted 8 columns, 22-29. It is punched as an unsigned fixed point decimal quantity, with two digits after the decimal point. e.g. 00046.52.

Now as an example, suppose we punch plane $(11,\bar{1},0)$ which has a structure factor of 4.3, and we wish to assign to it a weight of 1/5. Then the information would be punched on the first 29 columns of a decimal card as follows:

+ 11.0 - 01.0 + 00.0 0.2000 00004.30

N.B. There should be no blank columns between different numbers.

Program 2 - INPUT

Input to Program 2 is in two media, decimal cards and binary tape 3. The binary tape has been discussed under Program 1.

Decimal Cards

If there are N independent atoms in the asymmetric unit, then there will be (2N + 8) cards to be introduced into the computer for Program 2. These will be discussed one by one in the order in which they must be read by the computer. The full FORMAT statement for the card reading is:

FORMAT(I4/I2/I2/I2/I2/10I2/F8.4/4F6.4/(6E12.5/3F7.5)).

Card 1-I4

Card 1 carries the total number of planes being considered. This should be a four digit decimal integer punched in columns 1-4, e.g. 0154.

Card 2-I2

Card 2 carries the total number of atoms in the asymmetric unit. This should be a two digit decimal integer punched in columns 1 and 2. It should not at present be greater than 40, e.g. 09,21.

Card 3-I2

Card 3 carries the number of chemically different atom types in the asymmetric unit. This should be a two

digit decimal integer, not greater than 10, and should be punched in columns 1 and 2 of the card. e.g. 03, 06, 10.

Card 4-I2

Card 4 carries the number assigned to the atom at which refinement of temperature parameters should begin. This should be a two digit decimal integer punched in columns 1 and 2 of the card, e.g. 01, 02, 09, 15. This provision is introduced in order to permit the refinement of the parameters of selected atoms only.

Card 5-I2

Card 5 carries the number assigned to the atom at which refinement of atomic coordinates should begin. This should be a two digit number punched in columns 1 and 2 of the card, e.g. 01, 02, 09, 15. This provision is introduced in order to permit the refinement of the coordinates of selected atoms only; this is particularly desirable where some atoms are in special positions.

Card 6-10I2

Card 6 carries ten two-digit decimal numbers, punched in columns 1-20. These numbers represent the numbers assigned to the LAST ATOM OF A GIVEN CHEMICAL TYPE. The

numbers are used by the computer, in the calculation of structure factors and differentials, to recognize when to use a different scattering factor.
Consider once again the case of $CuSO_4.H_2O$ mentioned in connection with Program 1.

Atom 1	Cu
Atom 2	S
Atoms 3–7	O
Atoms 8–9	H

There are four different types of atom here. Therefore the numbers punched on card 6 are:

01, 02, 07, 09, 00, 00, 00, 00, 00, 00.

Where there are fewer than ten atom types the remaining columns up to twenty MUST be punched with zeros.

Card 7–F8.4

On card 7 is punched the initial value of the scale factor, SC, as defined on page 3. It is punched as a fixed point decimal quantity in columns 1–8, with four places after the decimal point, e.g. -02.3651.

Card 8– 4F6.4

Card 8 carries damping factors which may be applied to the corrections obtained from the least squares

procedure. The damping factor applied to temperature parameters is punched in columns 1-6, that applied to the x-coordinates in columns 7-12, that applies to the y-coordinates in columns 13-18, and that applied to the z-coordinates in columns 19-24. These are punched as fixed point decimal quantities with four integers after the decimal point, e.g. 0.7500.

Remaining 2N cards

The remaining cards are arranged in pairs, one pair for each atom. The pairs should be arranged in such a way that the cards are read in the order in which the atoms have been numbered.

First card of pair - 6E12.5

The first card of each pair carries the initial values of the six anisotropic temperature parameters of each atom. These are punched as floating point decimal quantities with five significant figures, e.g. +0.96543E-03

is punched in columns 1-12
is punched in columns 13-24
is punched in columns 25-36
is punched in columns 37-48
is punched in columns 49-60
is punched in columns 61-72

If the value of any of these parameters is zero, then this must also be punched in the same format: e.g. 0.00000 E + 00.

Second Card of pair 3F7.5

This carries the x,y,z coordinates of the atom in terms of fractions of the unit cell edges. They are expressed as signed fixed point decimal quantities with 5 digits after the decimal point. (N.B. Since the value of these parameters cannot be greater than 0.99999, no provision is made for punching a digit before the decimal point).

e.g. - .73620

x-coordinate is punched in columns 1-7
y-coordinate is punched in columns 8-14
z-coordinate is punched in columns 15-21.

Once again, it should be emphasized that no blank columns should be left between numbers on the same card.

Program 2 - OUTPUT

The output from program 2 is written entirely on Tape 4 in BCD. However some quantities are printed

out on the attached printer as well, in order to allow the operator to observe the progress of the refinement. The tape is NOT written under program control, and the peripheral printer should be set to single or double spacing.

Tape 4

When sense switch 1 is DOWN, i.e. when structure factors only are calculated, then on Tape 4 are written the values of h,k,l Fo,Fc, and Fo-Fc, for each reflection.

When sense switch 1 is UP and a refinement is proceeding, then the following quantities are written on Tape 4.

a) Average correction to temperature parameters

$$= \frac{\sum|\text{corrections}|}{\sum|\text{parameters}|}$$

b) Average correction to coordinates $= \frac{\sum|\text{corrections}|}{\sum|\text{coordinates}|}$

c) New scale factor.

d) Atom number - New value of temperature parameters for that atom - New values of coordinates of that atom.

This last step is repeated for all atoms, even those whose variables are not being refined.

Printer

At the end of each cycle of refinement the following quantities are printed out on the attached printer.

a) Average correction to the temperature parameters

b) Average correction to the coordinates

c) New scale factor:

By manipulation of the sense switches as described later the following quantities are printed out.

a) Discrepancy $\left(R = \frac{\sum||Fo| - |Fc||}{\sum|Fc|}\right.$

b) $R^1 = \sum(|Fo| - |Fc|)^2$

SENSE SWITCHES

The nature of the refinement carried out by the program is controlled by the sense switches. The effect of the sense switches may be briefly summarized:

Sense switch 1 - DOWN - calculates Fc only.

Sense switch 2 - DOWN - thermal parameters refined only.

Sense switch 3 - DOWN - atomic coordinates refined only.

If switches 1, 2, and 3 are all up, thermal parameters and atomic coordinates are refined simultaneously.

If 1 or 2 or 3 is down, then the other two should be up.

Sense switch 5 - DOWN - Recycle

Sense switch 5 - UP - Goes to end of program.

Recycling

At present recycling is rather a complex business. After one cycle of refinement the average corrections to the parameters are printed out on line and the computer stops with HPR 77770 in the storage register of the computer.

If it is desired to carry out another cycle of refinement, sense switch 5 should now be set at the DOWN position. Pressing the START button causes R and R prime to be printed on line. (N.B. In refinement cycles, R and R prime are always 1 cycle behind when printed out; at the end of the refinements, a structure factor calculation brings R and R prime up to date). The computer then stops with HPR 77700 in the storage register. Pressing the START button twice now sets the computer going on another cycle as controlled by the setting of switches 1, 2, or 3.